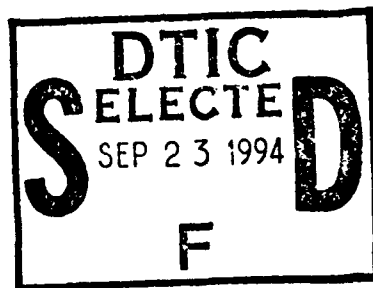


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**MODELING OF GROUND WATER AQUIFER
REMEDATION BY PULSED PUMPING WHEN
CONTAMINANT TRANSPORT IS AFFECTED BY
PHYSICAL, NON-EQUILIBRIUM
SORPTION AND DESORPTION**

THESIS

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AFIT/GEE/ENC/94S-01

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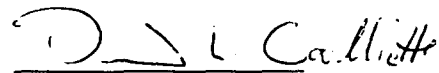
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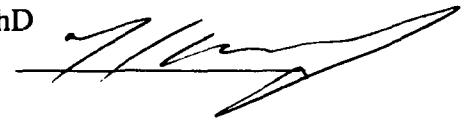
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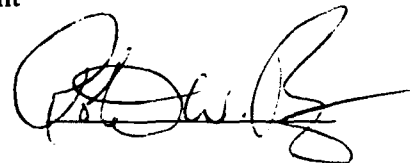


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**MODELING OF GROUND WATER AQUIFER REMEDIATION BY PULSED
PUMPING WHEN CONTAMINANT TRANSPORT IS AFFECTED BY
PHYSICAL, NON-EQUILIBRIUM SORPTION AND DESORPTION**

THESIS

**Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air Education and Training Command
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in
Engineering and Environmental Management**

**Jeffrey L. Caspers
Major, United States Marine Corps**

August 1994

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Preface

I thank God for the mental stamina and His providential grace, as well as the intercessory prayers and encouragement from family, friends and fellow believers in undertaking and completing this project. I hope that my research efforts in the field of modeling of contaminant transport will contribute additional insight in studying this complex phenomena and application in field modeling.

I am greatly indebted to my faculty advisor, Major David L. Coulliette, U.S. Air Force, without whose guidance, infinite patience, encouragement and countless hours of reviewing various concepts, finite element theory and computer coding this thesis would not have been possible. I would also like to extend my deepest appreciation to my committee members, Lieutenant Colonel Michael L. Shelley, U.S. Air Force and Dr. Robert W. Ritzi during this undertaking. Their patience and support in reviewing ground water concepts, remediation methods, contribution of emergent literature and validation techniques for the model ensured proper focus and application of my efforts.

A word of appreciation is also due to Lieutenant Colonel Mark N. Goltz, U.S. Air Force (Retired) who provided encouragement and reality checks on rate-limited sorption at critical phases of the model development and in analysis of simulation results. Additionally, Dr. Charles Bleckmann and Dr. Kirk A. Mathews contributed significant observations, physically and theoretically, which helped to explain the functioning of the model in more simplistic terms for me. Captain Thomas A. Adams, U.S. Air Force also contributed significantly throughout this research with his introduction to the literature

used in his thesis, coaching me throughout, and in setting up his latest version of his analytical code to validate this modification.

Not to be forgotten are the patient and innovative efforts of the "SC" gang and a SOCHE student, Jim Stamper, who cobbled computer systems together through frequent system interruptions, taught advanced computing techniques to one who was initially illiterate, and brought me up to speed on the intricacies of the SUTRA code. Their support and systems monitoring were absolutely crucial when regenerating simulation runs in the latter phases of this research.

Finally, my most heartfelt thanks goes to my wife, Anita Caspers and my sons, Philip, Jonathon, Matthew and David. This thesis has taken an enormous amount of time and without their love, prayers and mutual sacrifice in what turned out to be a major disruption in their lives following my previous tours of combat duty, I would have never endured its demands. I owe them a lifetime of gratitude and love for their selfless sacrifice of time and companionship in making this effort possible.

Table of Contents

	Page
Preface.....	ii
List of Figures.....	vii
List of Tables	x
List of Symbols.....	xi
Abstract.....	xv
 I. Introduction	 1-1
Background	1-1
Specific Problem.....	1-7
Research Objectives.....	1-7
Scope and Limitations.....	1-8
Definitions.....	1-9
Overview.....	1-13
 II. Literature Review	 2-1
Overview.....	2-1
Contaminant Transport Processes.....	2-4
Sorption Isotherm Linearity	2-4
Linear/Nonlinear Isotherms	2-8
LEA Validity.....	2-10
Sorption Non-Equilibrium	2-11
Non-Equilibrium Sorption Models	2-12
Physical Non-Equilibrium Models	2-12
First-Order Rate Model.....	2-13
Diffusion Model With Ficks Law	2-16
Pore Geometry	2-19
Chemical Non-Equilibrium Model	2-20
Multi-Process Non-Equilibrium Model	2-21
Pump and Treat Systems.....	2-22
General.....	2-22
Continuous Pumping.....	2-24

Pulsed Pumping	2-26
Summary	2-27
III. SUTRA Model Modification	3-1
Introduction.....	3-1
SUTRA	3-1
General	3-1
SUTRA Numerical Methods.....	3-2
Physical-Mathematical Basis of SUTRA Simulation	3-2
Water Mass Balance Governing Equations	3-3
Contaminant Transport Equation.....	3-10
Advection, Dispersion and Diffusion	3-11
Equilibrium Sorption Isotherms.....	3-13
Sources and Sinks Within the Liquid Phase	3-13
Solute Mass Additions	3-14
Implementing Non-Equilibrium Sorption in SUTRA	3-14
General	3-14
First Order, Non-Equilibrium Assumption	3-17
Second- Order, Non-Equilibrium Assumption	3-18
Iterative Solution Scheme	3-19
IV. Analysis and Evaluation of Results	4-1
Introduction.....	4-1
Validation of Model Modifications	4-1
Introduction.....	4-1
Radial Test Input Parameters	4-3
Results of Validation.....	4-4
Model Aquifer Parameters	4-5
General	4-5
Validation of Non-Equilibrium Regime	4-6
Finite Element Mesh.....	4-6
Immobile Region Mesh.....	4-8
Boundary Conditions	4-9
Initial Contaminant Plume	4-10
Aquifer Remediation.....	4-11
General	4-11
Criteria to Define Aquifer Cleanup.....	4-12
LEA Model	4-12
Non-Equilibrium Model.....	4-13
Comparing Aquifer Remediation Strategies	4-13
Non-Equilibrium Effects on Breakthrough Curves	4-14

First- and Second-Order Pulsed Pumping Comparison	4-14
General	4-14
Pore Volume Analysis	4-15
Spherical Diffusion	4-18
Small D_e/a^2 Ratio Comparison At A Higher Pumping Rate.....	4-22
Large D_e/a^2 Ratio Case Comparison.....	4-28
Summary	4-33
Pumping Strategy Comparison	4-34
 V. Conclusions and Recommendations	5-1
Overview.....	5-1
Summary of Findings.....	5-3
Recommendations.....	5-4
 Appendix A: Radial Pumping Test Input Parameters.....	A-1
Appendix B: Representative Sandy Aquifer Input Parameters.....	B-1
Appendix C: Immobile Region Finite Element Mesh	C-1
Appendix D: Breakthrough Curves	D-1
Appendix E: First-Order Pulsed Pumping Strategies	E-1
Appendix F: Second-Order Pulsed Pumping Strategies	F-1
Bibliography	BIB-1
Vita.....	VITA-1

List of Figures

<u>Figure</u>	<u>Page</u>
2.1	Bicontinuum Model for Contaminant Transport 2-5
2.2	Example of Tailing During Pump-and-Treat Remediation..... 2-25
2.3	Conventional Pump-and-Treat With Rebound 2-26
2.4	Pulsed Pumping of Residuals..... 2-27
3.1	Mass Balance in a Cubic Element in Space 3-4
3.2	Dual Porosity Media-Spherical Blocks 3-15
3.3	Discretization of Spherical Immobile Region 3-16
4.1	Finite Element Mesh and 2-D Boundary Conditions for Hypothetical Model 4-8
4.2	Initial Contaminant Plume for Hypothetical 2-D Ground Water Model 4-11
4.3	Low Pumping Rate Immobile Region Concentration Profiles..... ($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)..... 4-19
4.4	First- and Second-Order, Pulsed Pumping Comparison to LEA Model..... ($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)..... 4-21
4.5	First- and Second-Order, Pulsed Pumping Comparison to LEA Model..... ($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)..... 4-21
4.6	First- and Second-Order, Pulsed Pumping Comparison to LEA Model..... ($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)..... 4-22
4.7	SUTRA Unmodified Comparison to Second-Order Diffusion Model ($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)..... 4-24
4.8	First- and Second-Order, Pulsed Pumping Comparison to LEA Model..... ($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)..... 4-25

4.9	High Pumping Rate Immobile Region Concentration Profiles	
	($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$).....	4-28
4.10	First- and Second-Order, Pulsed Pumping Comparison to LEA Model	
	($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$).....	4-30
4.11	Low Pumping Rate Immobile Region Concentration Profiles.....	
	($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$).....	4-31
4.12	First- and Second-Order, Pulsed Pumping Comparison to LEA Model	
	($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$).....	4-31
4.13	First- and Second-Order, Pulsed Pumping Comparison to LEA Model	
	($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$).....	4-32
4.14	High Pumping Rate Immobile Region Concentration Profiles	
	($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$).....	4-32
4.15	Pumping Strategy Comparison ($D_e/a^2 = 0.005$)	4-35
D.1	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.009$).....	D-1
D.2	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.009$).....	D-1
D.3	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.009$).....	D-2
D.4	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.013$).....	D-2
D.5	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.013$).....	D-3
D.6	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.013$).....	D-3
D.7	Comparison of First- and Second-Order Diffusion Models to LEA.....	
	($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.014$).....	D-4
D.8	Comparison of First- and Second-Order Diffusion Models to LEA.....	

	(Q = 400 m ³ /day) ($D_e/a^2 = 0.014$).....	D-4
D.9	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 600 m ³ /day) ($D_e/a^2 = 0.014$).....	D-5
D.10	Comparison of First- and Second Order Diffusion Models to LEA (Q = 100 m ³ /day) ($D_e/a^2 = 0.025$).....	D-5
D.11	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 400 m ³ /day) ($D_e/a^2 = 0.025$).....	D-6
D.12	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 600 m ³ /day) ($D_e/a^2 = 0.025$)	D-6
D.13	Comparison of First- and Second-Order Diffusion Models to LEA. (Q = 100 m ³ /day) ($D_e/a^2 = 0.039$).....	D-7
D.14	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 400 m ³ /day) ($D_e/a^2 = 0.039$).....	D-7
D.15	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 600 m ³ /day) ($D_e/a^2 = 0.039$).....	D-8
D.16	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 100 m ³ /day) ($D_e/a^2 = 0.12$).....	D-8
D.17	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 400 m ³ /day) ($D_e/a^2 = 0.12$).....	D-9
D.18	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 600 m ³ /day) ($D_e/a^2 = 0.12$).....	D-9
D.19	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 100 m ³ /day) ($D_e/a^2 = 0.225$).....	D-10
D.20	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 400 m ³ /day) ($D_e/a^2 = 0.225$).....	D-10
D.14	Comparison of First- and Second-Order Diffusion Models to LEA..... (Q = 600 m ³ /day) ($D_e/a^2 = 0.225$).....	D-11

List of Tables

<u>Table</u>	<u>Page</u>
2.1 Adsorption Isotherms.....	2-8
4.1 Comparison of First- and Second-Order Nodes to Analytical Model	4-5
4.2 Comparative Rest Periods for D_e/a^2 Ratios and First-Order Rate Constants.....	4-16
4.3 Comparison of Extracted Pore Volume to Achieve Cleanup	4-17
4.4 Cleanup Time For Low D_e/a^2 Ratio (0.005)	4-28
4.5 Cleanup Time for High D_e/a^2 Ratio (0.005)	4-33
4.6 Mass Extraction Pumping Strategies	4-37

List of Symbols

a	Immobile region radius [L]
b	Aquifer thickness [L]
b_i	Maximum capacity of sorbed solute
C	Contaminant aqueous concentration [M/L ³]
C^*	Additional contaminant source aqueous concentration [M/L ³]
C_a	Local solute concentration at points within the immobile region [M/L ³]
C_i	Dissolved species concentration [M/L ³]
C_{im}	Volume-averaged immobile region solute concentration [M/L ³]
C_m	Mobile region solute concentration [M/L ³]
C_o	Base fluid solute concentration [M/L ³]
C_R	Solute concentration in water injected into the medium [M/L ³]
D	Coefficient of mechanical dispersion [L ² /T]
D_d^*	Coefficient of molecular diffusion [L ² /T]
D_d'	Effective diffusion coefficient [L ² /T]
D_e	Immobile region solute diffusion coefficient [L ² /T]
D_m	Mobile region dispersion coefficient [L ² /T]
D_o	Liquid diffusion coefficient
F	Mass of solute adsorbed on the solid per unit mass of solid
f	Volumetric adsorbate source
f	Fraction of sorption sites in direct contact with mobile water
f_{oc}	Fraction of organic carbon within the soil matrix
f_s	Specific sorption rate
g	Gravitational acceleration [L/T ²]
h	Head [L]
k	Intrinsic permeability [L ²]

k	solid matrix permeability [L^2]
k_r	Relative permeability to fluid flow [L^2]
k_1	Dimensionless forward reaction rate constant
k_2	Dimensionless backward reaction rate constant
K	Hydraulic conductivity of the matrix [L/T]
K_d	Partition coefficient between soil and water $[(M/M)/(M/L^3)]$
K_{oc}	Organic carbon partition coefficient
K_{ow}	Octanol-water partition coefficient
n	Intra-aggregate bulk porosity of the soil matrix [%]
P	Rate of water withdrawn at a pumping well [L^3/T]
p	Fluid pressure [$M/L-T^2$]
p_w	Force of water pressure in the soil matrix [$M/L-T^2$]
q	Darcy velocity [L/T]
$q_{c,total}$	Total flux [L/T]
Q	Volumetric flow rate [L^3/T]
Q_p	Fluid mass source [L^3/T]
r	Pore radius [L]
r_p	Plume radius [L]
R	Dimensionless retardation factor
R_{im}	Retardation coefficient for the immobile region
R_m	Retardation coefficient for the mobile region
R_Q	Rate of water added at an injection well [L^3/T]
S	Mass of solute adsorbed per unit dry mass of soil [M/M]
S_{op}	Specific mass storativity [L^{-1}]
S_{op}^*	Specific mass Storativity of Change []
S_w	Water saturation index for the soil [%]
T	Solute mass source

t	Time [T]
\bar{v}	Average fluid velocity [L/T]
\bar{v}_m	Average pore-water velocity in the mobile liquid [L/T]
\bar{v}_s	Average velocity of solid in matrix [L/T]
x	Distance in flow direction [L]
z	Elevation of point above a given datum [L]

Greek Letters

β	Coefficient of compressibility of water [L-T ² /M]
ρ'	Bulk density of soil [M/L ³]
ρ	Fluid density [M/L ³]
ρ_s	Dry solid density [M/L ³]
ρ_w	Density of water [M/L ³]
θ	Volumetric moisture content [%]
θ_{im}	Fraction of the soil filled with stagnant water [L ³ /L ³]
θ_m	Fraction of the soil filled with mobile water [L ³ /L ³]
θ_s	Solid's volumetric fraction [%]
α	First-order mass transfer rate coefficient [T ⁻¹]
α'	Aquifer matrix compressibility [L-T ² /M]
μ	Fluid dynamic viscosity [M/L ² -T ²]
μ_w	Dynamic viscosity of water [M/L-T]
γ	Specific weight of fluid [M/L ² -T ²]
γ_w	Specific weight of water [M/L ² -T ²]
χ	Dimensionless second-rank tensor representing toruosity
Γ	Decaying species sink term

Γ_s	Sink term for rate of production of the solute per unit mass of solid
∇_p	Pore Volume [L^3]
∇_T	Total volume of the soil matrix [L^3]
∇_v	Volume of voids within the solid matrix [L^3]
∇_w	Volume of water within the matrix [L^3]

Abstract

This research postulates and demonstrates a modification incorporating rate-limited sorption effects in the USGS SUTRA code for cleanup of a hypothetical sandy aquifer by pump-and-treat remediation methods. Contaminant transport is assumed to be affected by advection, dispersion, and rate-limited sorption/desorption. Sorption is assumed to be either equilibrium or rate-limited, with the rate-limitation described by either a first-order law, or by Fickian diffusion of contaminant through a spherical immobile pore region. Solutions are arrived at by split operator methods for the transport and one-dimensional Galerkin solutions for the solute concentration equations. The resulting model is tested against an analytical Laplace transform model for both first- and Fickian diffusion methods in a radial pumping simulation. Model simulations are used to evaluate equilibrium, first-order and Fickian diffusion effects for pulsed and continuous pumping solutions within a hypothetical aquifer. These show that equilibrium methods under-predicted rebound, while first-order methods may under- and over-predict rebound within the matrix for certain regions and may be equivalent to Fickian diffusion in equilibrium regimes for cleanup time prediction. Model simulations are then used to show the efficiency of pulsed pumping methods in cleanup mass extraction per pumped volume for a contaminated aquifer pump-and-treat remediation activity versus more conventional, continuous pumping methods.

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I. Introduction

Background

Ground water is the source of drinking water for approximately 48,000 communities and twelve million individuals across the country. Almost all rural households (95%) and 50% of the general population depend upon ground water as their primary drinking water source [Jensen, 1993:250]. Spills or leaks of organic chemicals to the environment frequently result in the contamination of subsurface soils and ground water [Powers and others, 1991:463]. The 1989 Toxic Release Inventory by the Environmental Protection Agency (EPA) concluded that 11% of toxic chemical releases occurred on land. More significantly, 14% of the releases were underground [U.S. EPA, 1989b:173]. The widespread contamination of ground water due to years of accidental or deliberate disposal of various chemicals, particularly where contaminant plumes are encroaching on production or sole-source aquifers for ground water, is a growing issue within the United States.

Ground water contamination exists at more than 85% of the 1208 sites included on the National Priority List (NPL). Further, over 33,000 other sites have been identified and included in the Comprehensive Environmental Response, Compensation, and Liability Information System for ranking and potential inclusion on the NPL. Contaminant release

to ground water has been identified or is suspected at more than 1700 Resource Conservation and Recovery Act facilities. These sites, in addition to the large number of leaking underground storage tank sites and hazardous waste landfills with unlined or ruptured liners, has resulted in an enormous (ground water) contamination problem [Olsen and Kavanaugh, 1993:42]. In response, the Air Force is engaging in a program to identify, assess, and remediate hazardous waste sites at military installations throughout the United States [Goltz, 1991b:24].

Laboratory researchers, hydro-geologists and soil scientists have actively pursued modeling methods and technologies for remediation of ground water for years. The ability to predict rate of solute migration in ground water systems is critical to the evaluation of potential effects on water quality resulting from subsurface disposal of hazardous wastes, as well as in the design of measures to restore water quality of contaminated aquifers [Bahr and Rubin, 1987:438]. Due to the rising costs in performing aquifer remediation, it is important that decisions made regarding ground water cleanup be based upon the best available information [Adams and Virmontes, 1993:1-2]. One major source of information provided to the Installation Restoration Program (IRP) decision maker comes from contaminant transport models [Goltz, 1991b:24].

Almost all remediation of ground water at contaminated sites is based on ground water extraction by wells or drains [Mackay and Cherry, 1989:630; Goltz, 1991b:25; Haley and others, 1991:119; Hall and Johnson, 1992:216]. This is usually accompanied by treatment of the extracted water prior to discharge. Several trends in the effectiveness of this process have been observed in the field over time [Mackay and Cherry, 1989:630; Haley and others, 1991:119; Olsen and Kavanaugh, 1993:44]:

- (1) containment of ground water plumes was usually achieved;
- (2) contaminant concentrations dropped significantly, initially, followed by a leveling out and;
- (3) after the period of initial rapid decline, the continued decreases in concentration were usually slower than anticipated (sometimes for decades).

Contaminant transport is usually modeled by the advection/dispersion equation [Goltz, 1986a:1] in the mobile fluid region, with a diffusion model often representing contaminant transport within the immobile flow/soil matrix region. The transfer of contaminant between the flowing ground water and the soil matrix is modeled by the addition of a sink term in the advection/dispersion equation. This process will be referred to as "sorption" [Miller and Weber, 1988:466].

The model is significantly simplified if one assumes equilibrium exists between the mobile and immobile regions within the soil matrix. Most theoretical and mathematical models make an assumption that local equilibrium (LEA) is occurring within the macro or micro-pores of the soil [Brusseau, 1992b:353]. In this case the solute is assumed to be sorbed in an instantaneous, linear and reversible manner [Goltz, 1986a:2]. If the microscopic processes are "fast enough" with respect to the bulk flow rate, then reversible sorption reactions are assumed to be in a state of local equilibrium [Valocchi, 1985:808].

Models used to predict transport of solutes that assume equilibrium sorption can predict movement, in most cases, in large scale aquifers where bulk flow rates are slow [Szczesody, 1988:1]. However, other authors have demonstrated that a LEA model may

significantly underestimate the size of a plume of reacting solute for which the rate of sorption is limited by non-equilibrium mass transfer [Bahr and Rubin, 1987:438]. Several laboratory and field studies have indicated that LEA may not be adequate for simulating contaminant transport under some flow conditions [Valocchi, 1985:808; Yu, 1985:355; Valocchi, 1986:1696; Goltz and Roberts, 1986c:1139; Mackay and others, 1986:2047; Brusseau and Rao, 1989d:41; Brogan, 1991:165; Goltz, 1991b:24; Weber and others, 1991:505]. While local equilibrium may exist between the mobile and immobile zone concentrations in soil pores under natural flow fields, the increase in pore water velocities associated with pumping of the aquifer can often introduce or increase significantly, non-equilibrium conditions [Brogan, 1991:2].

Non-equilibrium sorption arises when physical and chemical processes at the single pore level are slow relative to advection in the bulk media [Szecsody, 1988:1]. The chemical binding and release of solute onto porous and solid particles within the soil matrix cause this to occur. The rate of sorption is controlled by one of three possible rate-limiting steps [Szecsody, 1988:9]:

- (1) diffusion through immobile fluid,
- (2) diffusion through organic matter, and,
- (3) chemical binding and release.

Non-equilibrium models have been introduced to better characterize these conditions. These models are based on the assumption that, either for physical or chemical reasons, adsorption does not proceed at an equal rate in all parts of the soil

medium [Van Genuchten, 1981:ii]. Conceptual models of non-equilibrium sorption in soils and aquifers are grouped into two classes: (1) physical non-equilibrium models, where the overall sorption rate is controlled by the rate at which the solute is transported to and from the reacting soil surfaces and (2) chemical non-equilibrium models where the overall sorption rate is equal to the rate of reaction at the soil-solution interfaces [Valocchi, 1986:1694; Grove and Stollenwerk, 1987:602-604].

The effects of non-equilibrium conditions, 'tailing' and 'rebound', have been observed in several laboratories and field studies. Tailing describes the asymptotic decrease in the rate of reduction of contaminant concentration in extracted water, after a relatively rapid initial decrease. Tailing is attributed to the slow diffusion of solute into zones of immobile water [Van Genuchten, 1981:3; Yu, 1985:355; Goltz, 1986a:5; Valocchi, 1986:1696; Goltz and Roberts, 1988:37]. Rebound involves the increase in contaminant concentration observed after cessation of pumping [Adams and Viramontes, 1993:1-4]. Rebound has been observed several years after the pump-and-treat system have been stopped and the hazardous site closed [Valocchi, 1986:1694; Mackay and Cherry, 1989:633; Goltz, 1991b:25]. Under these conditions, it appeared that contaminant in the sorbed and aqueous phases did not instantaneously equilibrate, but slowly reached equilibrium [Goltz and Oxley, 1991a:547].

Non-equilibrium solute transport is recognized as a key limitation to contaminant removal from ground water by "pump and treat" methods in recent literature [Valocchi, 1986:1699]. Slow sorption (with attendant tailing and rebound effects) of organic substances within the soil has resulted in long periods of treatment, sometimes in excess of that predicted by conventional modeling, with attendant costs. Additionally, such scenarios lead to potentially difficult pumping strategy determinations. In many situations,

continuous pumping did not prove to be practical [Mackay and Cherry, 1989:630; Haley and others, 1991:119; Olsen and Kavanaugh, 1993:44]. Processes observed to improve the plume capture and reduce quantities of water extracted, to reach the goal of "clean water," more efficiently, are referred to as "pulse pumping." Field experiments and modeling studies have demonstrated that this optimization of the process may achieve favorable results [Brogan, 1991:165; Haley and others, 1991:122; Goltz, 1991b:25; Haggerty, 1992:37; Adams and Virmontes, 1993:5-3].

An extensive survey [Van der Heijde and Elnawawy, 1993] of 142-mathematical models for ground water transport showed that 51 models use some form of an equilibrium or linear sorption routine to compute solute movement, and only three evaluate non-equilibrium sorption. Huso (1989), using finite elements, and Adams and Virmontes (1993) using an analytical model, modeled physical, non-equilibrium in radial, pulsed pumping tests. Brogan [1991:27] extensively modeled non-equilibrium solute transport and pulsed pumping for chemical (kinetic) non-equilibrium using a two-dimensional, reversible, first-order kinetic solute transport module addition to the public domain USGS code, SUTRA. Brogan's work was extended for multi-contaminant transport using modified, first-order kinetic computation equations, for faster computation [Haggerty, 1992:42-44].

SUTRA is a two-dimensional public domain code, which calculates subsurface ground water movement and contaminant transport in both the saturated and unsaturated zones. It models single species transport through a quadrilateral hybrid finite element transport model. Spatial derivatives are approximated with finite elements and temporal derivatives with finite differences [Voss, 1984:5-8]. A modification to SUTRA, for physical non-equilibrium, utilizing the two-region model equations developed by Van

Genuchten [1985:513] for both first- and second-order, non-equilibrium sorption will be investigated as a more rigorous approach towards modeling the physical processes within the soil than the chemical approach presented by Brogan.

Specific Problem

The purpose of this research is to mathematically model aquifer remediation by pulsed pumping when contaminant transport is affected by physical, diffusion, rate-limited sorption. This research will extend the work of Goltz and Oxley (1991a), Brogan (1991) and Adams and Virmontes (1993).

Research Objectives

The specific objectives of this research are to:

1. Develop and validate a modification to the SUTRA transport model that incorporates the mechanisms of advection, dispersion, and physical non-equilibrium sorption using a two-region model to emulate immobile regions within the soil matrix by multiple simulations. The study is limited to the special case where advection is due to steady ground water velocity.
2. Perform a comparison test with an existing analytical code for both first- and second-order, rate-limited sorption for a radial flow zone, simulated by a pumping well.
3. Compare and contrast solute extraction efficiency of the second-order, physical non-equilibrium sorption algorithm with first-order and an LEA model, for a pulsed-pumping remediation simulation.

4. Compare efficiency of contaminant extraction between continuous pumping strategies and pulsed pumping strategies through integration of breakthrough curves during extraction and comparison of contaminant mass extracted with the pumped water.

Scope and Limitations

Simplifying assumptions used in this research are listed below:

1. Single species, solute transport will be simulated.
2. Boundary conditions are constant throughout pumping and rest cycles.
3. Transport of the contaminant due to the natural ground water gradient is negligible during the period of extraction. Containment of the plume is not necessary to prevent the spread of ground water contamination to other areas (outside the representative volume to be studied). The extraction well must create a flow field that encompasses the area of the contaminant plume.
4. In the governing contaminant transport equation, molecular diffusion is negligible with respect to mechanical dispersion, when the pump is on.
5. The formation is homogenous. The vertical dimension is a fixed parameter. This facilitates SUTRA's three-dimensional characterization of the aquifer and plume.
6. The maximum concentration is located at the center of the plume, with the radius of the plume defined as the distance at which the concentration is 1% of the minimum action level.

7. Hydraulic head and contaminant concentration are both constant with respect to depth.
8. All water entering the aquifer from the boundaries is contaminant free.
9. It is not desirable to de-water the aquifer, nor to pump the well dry.

Definitions

Key terms associated with contaminant transport and aquifer remediation, as defined by the EPA unless otherwise specified, are listed below [Mercer and others, 1990; U.S. EPA, 1993].

1. **Absorption**: adherence of ions or molecules in solution to the surface of solids.
2. **Advection**: the process whereby solute is transported by the bulk mass of flowing fluid.
3. **Aquifer**: a geologic unit that contains sufficient saturated permeable material to transmit significant quantities of water.
4. **Aquitard**: a relatively impermeable layer that greatly restricts the movement of ground water [Freeze and Cherry, 1979:47].
5. **Breakthrough Curve (BTC)**: plot of contaminant concentration versus time relation at a particular point (spatially)[Freeze and Cherry, 1979:391].

6. Cleanup: the attainment of a specified contaminant concentration level [Goltz and Oxley, 1991a:547]; water quality or Safe Drinking Water Act Standard is sometimes used as the regulatory criteria to define cleanup of an aquifer. This concentration level is used to define the solute concentration criteria to define cleanup for this thesis. It is also necessary for solute concentrations to remain below this cleanup criterion after pumping has stopped.
7. Cleanup-mass: total mass of contaminant extracted by a pump-and-treat system as dissolved solute within the pumped ground water.
8. Cleanup-time: total time it takes to achieve cleanup [Brogan, 1991:82].
9. Cleanup-volume: total volume of ground water that is extracted from the aquifer [Brogan, 1991:82].
10. Concentration Gradient: movement of a contaminant from a region of higher concentration to one of lower concentration [Freeze and Cherry, 1979:25].
11. Contaminant Removal Efficiency: the amount of contaminant removed per volume of water pumped. This is the slope of the mass arrival curve [Brogan, 1991:40].
12. Desorption: the reverse of sorption.
13. Diffusion: mass transfer as a result of random motion of molecules. It is described by either a first-order equation of Ficks law of diffusion (second-order equation).

14. Dispersion: the spreading and mixing of the contaminant in ground water caused by diffusion and mixing due to microscopic variations in velocities within and between pores.
15. Effective Porosity: the ratio, usually expressed as a percentage, of the total volume of voids available for fluid transmission to the total volume of the porous medium.
16. Extraction Well: a pumped well used to remove contaminated ground water; operated solely during the pumping cycle and has the primary objective of removing contamination from the aquifer. The extraction well provides plume containment during the pumping cycle [Brogan, 1991:144].
17. Gradient Control Well: a pumped well used to remove contaminated ground water during the rest cycle with the objective of preventing off-site migration of the contaminant plume while desorption takes place [Brogan, 1991:144].
18. Heterogeneous: A geologic unit in which the hydrologic properties vary from point to point.
19. Homogeneous: a geologic unit in which the hydrologic properties are identical from point to point.
20. Mass Arrival Curve: a plot of the mass fraction removed versus the number of pore volumes pumped [Brogan, 1991:40].
21. Pulsed Pumping: a pump-and-treat enhancement where extraction wells are periodically not pumped to allow concentrations in the extracted water to increase.

22. Pumping Cycle: time period during which the extraction well is operating to remove contaminant mass from the ground water [Brogan, 1991:108].
23. Rebound: increase in contaminant concentration in the ground water that is observed due to desorption [Adams and Virmontes, 1993:1-4].
24. Rest Cycle: non-pumping period for the extraction well. It may include a pumping period for a gradient control well, where the objective is to allow solute concentrations to increase through desorption [Brogan, 1991: 108].
25. Retardation: the movement of a solute through a geologic medium at a velocity less than that of the flowing ground waters due to sorption or other removal of the solute.
26. Sorption: processes that remove solutes from the fluid phase and concentrate them on the solid phase of a medium; the generic term used to encompass the phenomena of adsorption and adsorption.
27. Tailing: the slow, nearly asymptotic decrease in contaminant concentration in water flushed through contaminated material.
28. Unconfined Aquifer: an aquifer in which the water table forms the upper boundary [Freeze and Cherry, 1979:48].

Overview

IRP planners use contaminant transport models to assess risk; to design remedies and to estimate remediation cost and cleanup time duration at IRP hazardous sites. Chapter I examined one modeling assumption often employed at these sites. It discussed how this assumption does not account for slow or non-equilibrium sorption/desorption that has been observed in several field and laboratory studies. A modification to the SUTRA program was proposed to evaluate a pulsed-pumping scheme as a technique to enhance the effectiveness of ground water pump-and-treat systems by accounting for physical non-equilibrium sorption in the soil matrix. This chapter concludes with a research proposal to validate a mathematical model of an aquifer decontamination by using pulsed-pumping when the contaminant transport is affected by physical non-equilibrium sorption and desorption.

Chapter II discusses the literature associated with sorbing solute transport modeling. An introduction to the basic equation used to represent solute transport in ground water is presented. Then, the chapter reviews the efforts of researchers to develop mathematical models to account for equilibrium and non-equilibrium sorption. A discussion follows on the validity of the respective regimes (equilibrium, versus non-equilibrium). Physical versus chemical (kinetic) non-equilibrium modeling of processes is then discussed. Finally, a discussion concerning the application of various pump-and-treat technologies (continuous pumping versus pulsed-pumping) is presented.

Chapter III presents a derivation of the Van Genuchten [1985] two-region model, as modified by Goltz and Oxley [Goltz and Oxley, 1991a; Goltz and Roberts, 1986b, c] for physical non-equilibrium and its application in modification of the SUTRA code to accommodate first- and second-order, rate-limited sorption within spherical aggregates.

These describe the contaminant transport by means of radial flow with sorption in an aquifer undergoing pulsed-pumping operations. Sorption/desorption is described assuming Fickian diffusion of the contaminant through immobile water in zones of spherical geometry.

In Chapter IV, we validate the modifications made to the SUTRA code for finite elements and differences with a previously validated analytical model [Adam's and Viramontes, 1993] which incorporates rate limited sorption and desorption. Breakthrough times, approach to equilibrium, rebound and cleanup time are compared for first- and second-order simulations with an LEA model for a range of parameters. Several breakthrough curves are generated and used to illustrate the simulations and model comparisons. We then analyze simulations of pulsed and continuous pumping schemes for optimal extraction efficiency. Cleanup time, mass and pore volumes extracted are computed and compared for pulsed, pump-and-treat remediation activities versus continuous pumping strategies in remediation of a hypothetical sandy aquifer.

Chapter V summarizes the research, draws conclusions based on the findings and offers recommendations for further research.

II. Literature Review

Overview

Hazardous waste remediation will become even more important in the future than at the present. As of 1970, the EPA estimated that 94% of the rural population and 37% of the public water supplies relied on ground water as their primary source [Canter and others, 1987:7]. An Office of Technology Assessment (OTA) estimate of major sources of potential ground water contamination include: hazardous waste sites (7,000); leaking underground storage tanks (75,000-100,000); industrial and municipal landfills (100,000) and septic tank systems (20 million) [Canter and others, 1987:67-90].

The United States is currently spending approximately \$10 billion annually on environmental cleanup and this is expected to rise to \$11.2 billion by 1999 for the Federal sector alone [Bredehoeft, 1994:97]. The 1992 Department of Defense (DOD) Authorization Act provided over \$1.4 billion for environmental restoration for all services. The Air Force has estimated that \$1.45 billion will be required to implement existing environmental interim agreements for remediation projects currently identified [DOD DERP, 1992:27, A-5].

A recent study of the Superfund National Priorities List (NPL) found that 46% of the NPL sites used pump-and-treat technology for collection and treatment [Bredehoeft, 1994:98] and 13% of DOD Installation Restoration Program (IRP) sites involved ground water treatment [DOD DERP, 1992:8]. The Air Force operates 331 installations and owns 13 contractor-operated plants, within which there are 3520 IRP sites currently open for remedial investigation or action [DOD DERP, 1992:6]. As outlined above, many of

the problems endemic to the civilian sector are equally prevalent at Air Force installations.

The four major source types of pollution of ground water for Air Force installations are

[Gorelick and others, 1993:32]:

- (1) leaking underground storage tanks;
- (2) leaking pipelines (including sewers);
- (3) spills or other major releases of liquids at the ground surface;
- (4) industrial operations.

The most common contaminants at Air Force sites which are being cleaned up under the IRP comprise three major contaminant groups [Gorelick and others, 1993:2-3]:

- (1) petroleum hydrocarbon contaminants, which usually include benzene, ethyl benzene, toluene and xylene,
- (2) trichloroethylene (TCE) and related solvents from degreasing, paint handling, metal plating and other similar operations,
- (3) toxic metals and other inorganic contaminants such as lead, cadmium, chromium and cyanide.

Given the ground water pollution problems in the civilian sector and similar ones being experienced at DOD installations under the IRP, it is important that modeling efforts

continue to better quantify and clarify the spatial and temporal characteristics of contaminant plumes, prior to initiation of expensive remediation projects. Accurate modeling of sorption processes is essential in assessing the effects of transport of sorbing organic solutes for optimization of pump-and-treat, treatment technology. According to recent estimates for the Superfund Program, the average per-site cost of characterization through initiation of remedial action for a pump-and-treat system is about \$14.1 million [Lee and Kitanidis, 1991:2203]. Given the expense of remediation, risk to public health, and time involved for clean-closing of a pump-and-treat site; the ability to model contaminant transport, both spatially and temporally may give critical insight towards design strategies which optimize the process of remediation.

Critical to this is the development of a mathematical model which can accurately simulate solute transport through the subsurface. Of the various transport processes, sorption is one of the most important; it is often the paramount process controlling the behavior of contaminants in the sub-surface under many conditions [Piwoni and Keeley, 1990:1]. Sorption results in solutes traveling slower than the water present in the aquifer [Thorbjarnarson and Mackay, 1994:401]. If sorption is linear, reversible and instantaneous, the solute transport can be modeled using simplistic methods, such as equilibrium transport. These simplifying assumptions are called the "Local Equilibrium Assumption (LEA)". However, these assumptions are not justified under all circumstances and non-equilibrium transport of organic solutes during pump-and-treat remediation of contaminated aquifers has lead to tailing of concentrations above typical clean-up goals for very long periods of time [Mackay and Cherry, 1989:630].

The effect of contaminant desorption from solids is to extend the time required to remove specified levels of contaminant for a given pumping rate due to retardation of the

contaminant plumes migration. Further, this retardation may require extraction of greater quantities of water than estimated under the LEA case, due to the desorption of contaminant from immobile zones (through diffusion processes) to mobile zones where "clean water" has replaced that removed during pumping [Mackay and Cherry, 1989:633; Hall and Johnson, 1992:218].

The analytical and mathematical modeling of the processes for non-equilibrium transport of organic solutes has received considerable attention over the past five-years. Modeling the processes that lead to non-equilibrium transport of organic solutes under field conditions, particularly forced-gradient pumping conditions such as those induced in most remediation efforts has received some emphasis of late from some researchers, notably Huso (1989), Brogan (1991), Adam's and Viramontes (1993) for single species transport and Haggerty (1992) for multi-species transport.

Contaminant Transport Processes

Sorption Isotherm Linearity

Mass transport is controlled by a variety of physical, chemical and biological processes. Quantitative descriptions of the advection and dispersion processes are well understood. Research emphasis has focused on diffusion and sorption processes, attempting to model these processes at the micropore level, and to account for the effects of tailing (slow desorption) of solute over long periods of time for certain solute and soil matrixes. Traditionally, three approaches have been taken in sorption modeling [Parker and Valocchi, 1986:399]:

(1) bicontinuum approach with interchange between mobile and immobile zones of specified geometry governed by Ficks Law for diffusion,

(2) bicontinuum approach with interchange described by an empirical first-order kinetic expression,

(3) equivalent monocontinuum approach which assumes residence times are sufficiently large to achieve negligible concentration differences between mobile and immobile pore regions (LEA).

Figure 2.1 illustrates the processes which are assumed to occur within the micropore zone for contaminant transport:

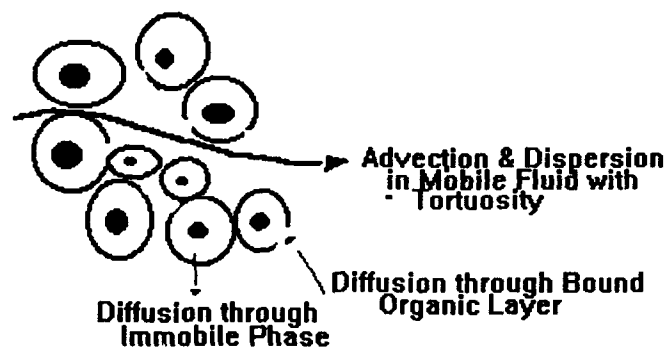


Figure 2.1. Bicontinuum Model for Contaminant Transport

The typical approach in modeling contaminant transport has been to assume conditions of local equilibrium [Bear, 1987:171; Brusseau and Rao, 1989d:34]. The conventional equation used to describe the advective-dispersive, one-dimensional transport of a sorbing solute is given by [Lapidus and Amundson, 1952:985; Van Genuchten, 1981:2]:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.1)$$

where C is the solute concentration in aqueous phase, θ is the volumetric moisture content, x is the distance in flow direction, D is the dispersion coefficient, ρ is the bulk density of soil, S is the mass of solute adsorbed per unit dry mass of soil, t is time and v is the average fluid velocity.

Describing the $\partial S / \partial t$ term is often the critical step in model formulation. The LEA results in the simplified expression:

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t} \quad (2.2)$$

where K_d is the partition coefficient between soil and water [Szecsody, 1988:3].

Upon substitution, the transport equation becomes:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (2.3)$$

where

$$R = 1 + \frac{\rho K_d}{\theta} \quad (2.4)$$

R is the retardation factor. Equation (2.3) will hereafter be referred to as the advective-dispersive (A-D) transport equation.

Advection is the movement of dissolved solute with flowing ground water. It is represented by the $v \frac{\partial C}{\partial x}$ term in the A-D equation. In coarse-grained, homogeneous aquifers, advective transport dominates the transport process. In the design of capture and containment systems, it is common to treat advection as the sole mechanism for contaminant transport [Gorelick and others, 1993:42].

The two processes that constitute hydrodynamic dispersion are molecular diffusion and mechanical dispersion. Molecular diffusion is the process in which dissolved contaminants move from areas of high concentration to areas of low concentration in response to the presence of a concentration gradient. Mechanical dispersion is the component of transport that results from the convoluted paths that water and contaminant particles follow while flowing through porous and fractured media (reflected by a tortuosity term)[Gorelick and others, 1993:42; Freeze and Cherry, 1979:75]. Diffusion and dispersion are included in the $D \frac{\partial^2 C}{\partial x^2}$ term in the A-D equation.

The physical significance of the retardation factor (Equation [2.4]) is that it measures how much slower the solute migrates than water because the solute spends part of its time sorbed on the soil matrix and is immobile [Charbeneau and others, 1992:43]. The higher the fraction of contaminant sorbed, the more retarded is its transport. If the sorptive reaction behaves linearly and is at equilibrium, the solute will move at an average velocity equal to the average linear velocity of the ground water flow divided by the retardation factor [Gorelick and others, 1993:44].

Linear/Nonlinear Isotherms

When LEA is applied, equilibrium is assumed to exist at each point in space between dissolved solute (associated with the liquid phase) and solute (associated through sorption), with the solid phases of the medium [Harmon and others, 1989:406], and is modeled using a partition coefficient as in Equation (2.2). As mentioned previously, this assumption greatly simplifies the transport model.

Linear isotherms are commonly used to model sorption in solute transport at low concentrations by assuming that a linear relationship exists between dissolved and sorbed solute [Harmon and others, 1989:407]. However, in many cases, linear models do not adequately describe the solute relationship. As a result, several non-linear relationships have been applied under the LEA. The commonly used isotherms are summarized in Table 2.1 below:

TABLE 2.1.
ADSORPTION ISOTHERMS

<u>Adsorption Isotherm</u>	<u>Equation</u>
Linear	$S = K_d C$
Freundlich	$S = K C^n$
Langmuir	$S = k_b C / (1 + k C)$
Langmuir Two-Surface	$S = (k_1 b_1 C / (1 + k_1 C)) + (k_2 b_2 C / (1 + k_2 C))$
Competitive Langmuir	$(C_1 / C_2) / S = (b_2 / k_1 b_1) + (C_1 / b_2 C_2)$

[Engesgaard and Christensen, 1988:192]

where S is the sorbed species; K_d is the distribution coefficient; K_i is the bond strength; C_i is the dissolved species concentration; k_1 and k_2 are the forward and

backward reaction rate constants [Carnahan and Remer, 1984:241] and b_i is the maximum capacity of sorbed solute.

For many nonionic compounds the Freundlich adsorption isotherm is typically used [Jury and Ghodrati, 1989:275; Pignatello, 1989:46]. Non-linearity is important for ionic or strongly polar compounds and is commonly modeled using the Langmuir isotherm [Brusseu and Rao, 1989d:38]. Linear sorption isotherms are frequently used where the distribution coefficient for the chemical species has been found to be a function of the hydrophobic character of the organic compound and the amount of organic matter present, using the equation [Charbeneau and others, 1992:42; Szecsody, 1989:3; Johnson and others, 1989:43]:

$$K_d = K_{oc} f_{oc} \quad (2.5)$$

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the fraction of organic carbon within the soil matrix.

The tailing effect on breakthrough curves results in a "spreading front" due to the slower, low concentration components of the plume lagging behind the faster moving, high concentration components of the contaminant plume. The tailing effect has been further explained by other authors [Hall and Johnson, 1992:218] as representing heterogeneities in permeability within the soil matrix, where pumping initially extracts contaminants from zones where advection dominates (larger open pores where fluid moves more readily) and where solute is retained in the smaller closed pores. Over time the contaminant in the closed pores is postulated to migrate to equilibrium with the concentration gradient in the open pores by a process of diffusion. This recharge of

contaminant within the open pores then causes the tailing effect explained mathematically above. The tailing effect serves to prolong the expected time of extraction of contaminant and increases the volume of water necessary for extraction and treatment [Mercer and others, 1990:8].

LEA Validity

As previously mentioned, LEA is a major component of the conventional solute-transport equation. If non-equilibrium conditions are present, LEA-based models will predict a breakthrough response that occurs too late and exhibits too little dispersion [Valocchi, 1985:808]. For the LEA to be valid, the rate of the sorption process must be fast relative to the other processes affecting solute concentration (e.g., advection, hydrodynamic dispersion) so that equilibrium may be established between the sorbing contaminant and the pore fluid [Bahr and Rubin, 1987:438; Engesgaard and Christensen, 1988:188; Brusseau and Rao, 1989d:41]. Additionally, other authors have described when the LEA applies as:

(1) when coefficient of hydrodynamic dispersion (D) was of same order of magnitude as the effective molecular diffusion coefficient (D_e) [Valocchi, 1985:808; Bahr and Rubin, 1987:438].

(2) when the limiting (smallest) Damkohler I ($D_a I$) number (an empirical relationship between the approach to local equilibrium and values of dimensionless parameters representing ratios of an average transit time to a reaction time) exceeds 100 [Bahr and Rubin, 1987:439; Brusseau and others, 1991b:1140-1141].

(3) when the chemical reaction of the solute is fast with respect to the bulk flow of fluid [Valocchi, 1985:808; Grove and Stollenwerk, 1987:603; Bahr and Rubin, 1987:438; Engesgaard and Christensen, 1988:188].

Sorption Non-Equilibrium

Sorption data from batch experiments have been found to exhibit a two-stage approach to equilibrium: a short initial phase of fast uptake, followed by an extended period of much slower uptake [Wu and Gschwend, 1986:724]. This was also observed during the Borden field test where long term increases in retardation were attributed to non-linear equilibrium behavior or non-equilibrium sorption-desorption [Roberts and others, 1986:2056; Bahr and Rubin, 1987:438].

Data from many laboratory experiments exhibit asymmetrical BTCs, with earlier breakthrough, increased time to reach complete breakthrough (i.e., breakthrough-front tailing) and increased time for complete desorption (i.e., elution-front tailing). A rate-limited non-equilibrium process has been postulated as being responsible for the early breakthrough and tailing that produces the asymmetry exhibited by BTCs influenced by non-equilibrium [Brusseau and Rao, 1989d:43]. The occurrence of sorption non-equilibrium increases solute dispersion. Hydrodynamic dispersion will tend to dominate under conditions of low pore-water velocities and in fine-grained, poorly aggregated media, whereas non-equilibrium induced dispersion tend to predominate for larger velocities and for large-scale aggregation [Brusseau and Rao, 1989d:43; Rao and others, 1980:1145].

Non-Equilibrium Sorption Models

Data exhibiting behavior that deviates from that predicted by the simple LEA model has been reported, thus challenging the validity of this approach. As previously stated, there are cases where equilibrium is not reached rapidly enough with respect to advective transport to allow use of A-D equations with equilibrium sorption. As outlined in Chapter I, non-equilibrium sorption and desorption in sub-surface media arises when physical and chemical processes at the single pore level are slow relative to advection in the bulk media [Szecsody, 1988:1]. Non-equilibrium sorption has been attributed to several factors [Brusseau and Rao, 1989d:33]:

- (1) kinetic sorption;
- (2) diffusive mass transfer resistance;
- (3) sorption-desorption non-singularity.

Physical Non-Equilibrium Models

Physical non-equilibrium is defined as the rate-limited sorption/desorption resulting from the existence of mass-transfer resistance [Brusseau and Rao, 1989d:62]. Some authors have postulated physical non-equilibrium models which hypothesize the existence of zones of immobile water which act as diffusion sources and sinks for solutes [Van Genuchten, 1985:513; Goltz and Roberts, 1986b:77; Szecsody, 1988:8; Brusseau and Rao, 1989d:45]. Further, these models can be described as either first-order rate models [Van Genuchten and Wierenga, 1976:474; Goltz and Roberts, 1986b:81] or second-order diffusion models [Van Genuchten and Wierenga, 1976:474; Rao and others, 1980:1139; Van Genuchten and others, 1984:335; Brusseau and Rao, 1989d:47]. For hydrophobic,

organic compounds, physical non-equilibrium and intra-organic matter diffusion have been identified as probable predominant factors causing non-ideality within the organic matter matrix [Brusseau, 1989a:vi].

Most physical non-equilibrium models incorporate a two-zone description of a porous medium, although some authors have postulated more regions. This divides the medium into an immobile zone and a mobile zone into which the solute diffuses. Transport in the mobile zone is governed by the advective-dispersion equation [Equation (2.3)], with the retardation adjusted to account for mobile zone sorption. Solute transfer between the mobile and immobile regions can be accounted for in three ways [Rao and others, 1980:1139-1140; Parker and Valocchi, 1986:399; Brusseau and Rao, 1989d:47]:

(1) explicitly, with a bicontinuum approach describing the interchange between the mobile and immobile zones governed by Ficks law of diffusive transfer,

(2) explicitly, with a bicontinuum approach with interchange described by an empirical first-order kinetic expression (this assumes that the immobile region is a completely mixed zone),

(3) implicitly, with a lumped dispersion coefficient that includes the effects of sink/source diffusion as a parameter which replaces the hydrodynamic dispersion coefficient (D) in the advection dispersion equation [Equation (2.3)].

First-Order Rate Model

The first-order rate model describes a two-zone porous medium in which complete mixing is assumed within the immobile region. This simplified model uses a linear

expression as the driving force approximation. Solute transfer is assumed to be a function of solute concentration differences between the mobile and immobile zones and is lumped into an empirical mass-transfer term to account for this gradient. These zones act as diffusion sources/sinks for solute flowing in the mobile regions [Goltz and Roberts, 1986b:81]. The model uses the following equations [Van Genuchten and Wierenga, 1976:474]:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial z^2} - v_m \theta_m \frac{\partial C_m}{\partial z} \quad (2.6)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (2.7)$$

where θ_m and θ_{im} are the fractions of the soil filled with mobile and stagnant water, respectively, C_m and C_{im} are the concentrations in both the mobile and stagnant regions, v_m is the average pore-water velocity in the mobile liquid, and α is the first order, mass transfer coefficient.

This model has been refined assuming linear, reversible, equilibrium sorption for solute within immobile zones, as well as for the "mobile" solute and performing a mass balance for solute in the mobile region by others [Goltz and Roberts, 1986b:81; Brusseau and Rao, 1989d:57; Harmon and others, 1989:412] to:

$$R_m \theta_m \frac{\partial C_m}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} - \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} \quad (2.8)$$

where D_m is the dispersion coefficient for the mobile zone, R_m and R_{im} are the retardation factors in the mobile and immobile zones, respectively, defined as:

$$R_m = 1 + \frac{f\rho K_d}{\theta_m} \quad (2.9)$$

and

$$R_{im} = 1 + \frac{\rho(1-f)K_d}{\theta_{im}} \quad (2.10)$$

where f is a certain fraction of sorption sites that are in direct contact with mobile water.

Returning to the discussion concerning the first order rate expression where we make the assumption that immobile water zones are perfectly mixed, Equation (2.7) becomes [Goltz and Roberts, 1986b:82; Harmon and others, 1989:412; Brusseau and Rao, 1989d:56; Brogan, 1991:7]:

$$\theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \quad (2.11)$$

A number of authors have shown that the first-order rate model closely approximates the tailing and asymmetric affects expected of non-equilibrium sorption in column breakthrough curves for certain parameters and conditions [Van Genuchten and Wierenga, 1976:479; Goltz and Roberts, 1986b:85; Van Genuchten and others, 1977:283; Brusseau and Rao, 1989d:55-56]. This model, like the first-order, kinetic non-equilibrium model which follows below, avoids dealing with pore geometry, which the more mathematically rigorous diffusion model uses with Ficks law of diffusion. Due to its simplicity, the first order rate model has been extensively used for modeling of physical non-equilibrium processes in the literature.

Diffusion Model With Ficks Law

The second type of physical non-equilibrium model is known as the diffusion model and incorporates Ficks law of diffusion rather than the empirical first-order formulation in Equations (2.8) or (2.11) [Brogan, 1991:8]. Molecular diffusion generally dominates microscopic mass transfer processes and in the liquid phase is controlled by Fickian (random) motion [Weber and others, 1991:513]. Several component mechanisms are involved in the solute-transfer process [Van Genuchten and Wierenga, 1976:473-474; Szecsody, 1988:2; Brusseau, 1989a:6]:

(1) advective-dispersive transport from bulk solution into the boundary layer of adsorbed water surrounding the soil matrix,

(2) diffusive transport across the adsorbed water (film diffusion),

(3) pore and/or surface diffusion within the immobile region (intra-aggregate diffusion and within dead-end pores).

The mobile phase is generally assumed to be well-mixed, thus minimizing the importance of intra-aggregate resistance within the mobile regions. All three components may be a rate-limiting step. Intra-aggregate diffusion is usually the transfer process designated as the rate-limiting step in sorption [Brusseau and Rao, 1989d:47]. Other authors [Crittenden and others, 1986:282] have demonstrated that intra-aggregate diffusion can be modeled either as pore or surface diffusion and that characteristic skewing of breakthrough curves for tailing matched experimental data.

For diffusion models, the advective-dispersion equation is still applicable. However, since this model allows for concentration gradients within the immobile zone (vice use of a perfectly mixed zone assumption of the first-order model), the immobile zone concentration value will represent a volume averaged solute concentration from within the immobile zone. The immobile zone is generally represented by a sphere [Goltz and Roberts, 1986c:1140]. The general equation describing transport in the mobile zone is [Van Genuchten, 1985:514; Goltz, 1986a:8; Goltz and Roberts, 1986b:81-83; Goltz and Roberts, 1986c:1140-1141; Goltz and Roberts, 1988:41]:

$$\theta_m R_m \frac{\partial C_m}{\partial t} + \theta_{im} R_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - \theta_m v_m \frac{\partial C_m}{\partial z} \quad (2.12)$$

and for diffusion into or out of spherical aggregates by [Parker and Valocchi, 1986:400]:

$$\frac{\partial C_a}{\partial t} = \frac{D_e}{r^2 R_{im}} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_a}{\partial r} \right] \quad (2.13)$$

giving the mean resident concentration in the spheres by:

$$C_{im} = (3/a^3) \int_0^a r^2 C_a dr \quad (2.14)$$

where θ_m and θ_{im} are the volumetric water contents of the inter-aggregate (macropore) and intra-aggregate (micropore) liquid phases, R_m and R_{im} are the retardation factors of the two regions, C_m and C_{im} are the average solution concentrations of the inter- and intra-aggregate liquid phases, respectively, D_m is the dispersion coefficient for transport through the macropore region, r is the radial coordinate within the immobile zone, a is the immobile region radius or layered half-

width, v_m is the average pore-water velocity of the macropore liquid phase, z is soil depth and t is time.

The diffusion coefficient for the immobile zone is given by [Wu and Gschwend, 1988:1373]:

$$D_e = \frac{D_m n^2}{(1-n)\rho_s K_p + n} = \frac{D_0}{\chi} \quad (2.15)$$

where n is the intra-aggregate porosity, ρ_s is the dry solid density, D_0 is the liquid diffusion coefficient, D_m is the molecular dispersion coefficient, K_p is a partition coefficient and χ is tortuosity.

Within certain constraints the first-order model has been shown to simulate spherical diffusion predictions, but not for all matrix geometries and non-equilibrium conditions [Rao and others, 1980:1145; Van Genuchten, 1985:523; Parker and Valocchi, 1986:407]. In fact, it may over-predict contaminant mass remaining within the matrix at high pumping rates [Goltz and Oxley, 1991a:554]. Thorbjarnarson [1990:148] postulated that the first-order, mass transfer model may not accurately simulate the diffusion process in situations of high flow (due to pore water velocity influence on the mass transfer coefficient [α]) or small sampling scale relative to the diffusion rate. Further, the first-order model relies on curve fitting to determine the mass transfer coefficient at varying velocities and is less amenable to be used in a predictive mode [Goltz and Roberts, 1986b:91]. Finally, the spherical diffusion model is more firmly founded on a physical basis and is more amenable to independent determination of parameters [Rao and others, 1980:1145; Goltz and Roberts, 1986b:89].

Pore Geometry

As stated above, a critical factor to the diffusion model is that it requires knowledge of the specific pore geometry within the immobile regions of the intra-aggregate matrix. The equations above assume intra-particle diffusion is occurring within an ideal spherical aggregate. Several authors have derived equivalent equations for diffusion within cylindrical [Van Genuchten and others, 1984:336; Rasmuson, 1985:1117], rectangular [Goltz, 1986a:12-13], or layered shape geometry's [Sudicky and Frind, 1982:1634; Rasmuson, 1985:1117].

True porous media, however, may be far from this idealization. In an attempt to apply the simplified model, Rao and others [1982:348], demonstrated that non-spherical aggregates can be represented by equivalent spheres. Additionally, a non-homogenous matrix of spheres could be characterized by a volumetric, weighted average for the spherical radius. These would have a nominal radius which gives a volume equivalent to that of the aggregate it represents [Crittenden and others, 1986:272]. Van Genuchten [1985:520] extended the physical diffusion model to more general conditions involving aggregates consisting of plane sheets, solid cylinders and rectangular prisms. He tabulated shape factors for these geometries, which could be used with analytical solutions of the advection-dispersion equation as modified for spherical diffusion.

Using chemical engineering techniques, another group of authors proposed a model to account for differing aggregate distributions which used a swelling crystal to account for size distribution within the matrix [Moharir and others, 1980:1795]. The effects of aggregate size distributions may be important at the field scale, however, other authors have observed that its affects may be ignored when the size distribution is sufficiently narrow [Brusseau and Rao, 1989d:55].

Chemical Non-Equilibrium Model

Empirical first-order models have been discussed by several authors [Lapidus and Amundson (1952); Cameron and Klute (1977); Rao and others (1985); Valocchi (1985); Brusseau and Rao (1989b); Brusseau and others (1991b); Brogan (1991); Haggerty (1992)]. In these models, non-equilibrium is assumed to be the result of a time-dependent sorption reaction at the sorbing surface [Brusseau and Rao, 1989d:43].

Cameron and Klute [1977] published a two-site model which assumed sorption sites were divided into two fractions, where one has adsorption occurring instantaneously and on the other fraction, it occurs in a time dependent manner. This combined the first-order chemical kinetic model with the linear equilibrium model. The equations for the sorbed component are written as [Cameron and Klute, 1977:183; Brusseau and Rao, 1989d:43; Brogan, 1991:12-13]:

$$\frac{\partial S_I}{\partial t} = FK_p \frac{\partial C}{\partial t} \quad (2.16)$$

$$\frac{\partial S_{II}}{\partial t} = \alpha[(1-F)K_p C - S_{II}] \quad (2.17)$$

where α is the mass-transfer coefficient for chemical two-site non equilibrium model, and where F is the fraction of immobile zone sites occupied by S_I .

Kinetic non-equilibrium formulations have been extended by other authors who developed a sorption, kinetically influenced term model (SKIT) which solves parallel derivations of LEA and kinetic non-equilibrium formulations for a given solute transport problem [Bahr and Rubin, 1987:439]. Others have developed a dual process (two-site)

model to simulate the BTC of PCE, which coupled two, non-equilibrium mechanisms, one associated with physical non-equilibrium and the other that represented one of several sorption-related processes (e.g., chemical non-equilibrium, intra-sorbent non-equilibrium diffusion, spatial variations in sorption) [Brusseau and Rao, 1989c:241]. Like the first-order physical, non-equilibrium model, the first-order, kinetic model does not rely on an actual description of the porous mediums structure [Brusseau, 1989a:16]. Nkedi-Kizza and others [1984:1123] have shown that a two-site, first-order kinetic non-equilibrium model is equivalent to the physical first-order rate model which uses mass transfer and linear sorption isotherms for simulating local equilibrium conditions. While the two first order rate methods have been shown to be mathematically equivalent, at local equilibrium, they have different effects upon the conservative solute breakthrough curves [Thorbjarnarson, 1990:16]. This is particularly relevant in the case of hydrophobic, but non-sorbing solutes. Additionally, this model has not been able to satisfactorily predict early breakthrough at higher velocities of breakthrough curves for some column experiments [Van Genuchten and Wierenga, 1976:475; Wu and Gschwend, 1986:717].

Multi-Process Non-Equilibrium Model

Breakthrough asymmetry may not be properly simulated by only one of the non-equilibrium processes. Recent research postulated that a new model that explicitly accounts for multiple processes of non-equilibrium operating in series or parallel can approximate bicontinuum models (physical non-equilibrium) for certain parameters [Brusseau and others, 1989b:1971]. This model was published with some errors, which although corrected in later publication [Brusseau and others, 1991c:657], have yet to correct mathematical comparisons with data validations which appeared in the original [Ball and others, 1991:654]. Nevertheless, an extension of this model was used to predict sorption, degradation and transport of a contaminant in a packed column experiment

[Brusseau and others, 1992a:180]. However, previous experimental results have not shown that kinetic processes contributed to the rate-limiting mechanism for non-ionic, low-polarity organic chemicals [Brusseau and Rao, 1991a:141; Szecsody, 1988:7-8]. However, they may be important for other organic chemicals such as pesticides [Brusseau and Rao, 1989e:1691; Brusseau and others, 1991a:134]. Finally, this MPNE model has yet to be tested adequately to support the author's assertions [Ball and others, 1991:653].

Pump and Treat Systems

General

When a site has been well characterized for hydrogeologic conditions and contaminant concentrations, alternatives for control and remediation can be selected and combined to provide an overall strategy for cleanup [Charbeneau and others, 1992:101]. There are many alternatives to choose from in handling ground water contamination problems, whether they be containment, excavation, pump-and-treat, vacuum extraction, bio-remediation or in-situ treatment [US. EPA, 1992:130; Canter and others, 1987:467-470; US. EPA, 1990:1; Gorelick and others, 1993:7]. The selection amongst alternative methods is beyond the scope of this discussion. Other authors [Repa and others, 1985:4-21 to 4-48; Canter and others, 1987:467-492; Brubaker and Stroo, 1992:167-168] provide general considerations for the selection of technologies current at the time of their writing.

Pump-and-treat ground water extraction is the most commonly used remedial technology for contaminated aquifers [Charbeneau and others, 1992:4; US. EPA, 1992:136; US. EPA, 1989a:E-1]. A general survey of 112 sites where pump-and-treat was planned or operating identified the following general conclusions [US. EPA, 1989a:E-1 to E-2]:

(1) the ground water extraction systems were generally effective in containing the contaminant plumes and were most effective at sites where underlying aquifers have high inter-granular hydraulic conductivity [Repa and others, 1985:5-1],

(2) significant removal of contaminant mass from the subsurface was achieved,

(3) contaminant concentrations usually decrease most rapidly soon after the initiation of extraction. After this initial reduction, the concentrations tended to level off and progressed towards the clean-up goal at a slower rate than expected.

As previously stated, several physical phenomena have been identified that tend to interfere with aquifer clean-up performance of pump-and-treat systems [US EPA, 1989a:1-2; US EPA, 1990:2]:

(1) adsorptive partitioning of contaminants between the ground water and the aquifer materials (which this thesis is designed to model),

(2) aquifer heterogeneity (I assume homogeneity for this study),

(3) low transmissivity of the aquifer (which I assume is high [greater than 10^{-5} cm/s] enough to enable selection of pump-and-treat as a viable option),

(4) low permeability zones which trap contaminants within the aquifer (which are neglected in this study due to assumption of homogeneity),

(5) immobile non-aqueous phase liquids (NAPLs) that may contribute to a miscible contaminant plume by prolonged dissolution by creation of a separate phase at residual saturation (in this instance pump-and-treat is rate-limited by how fast the NAPL components can dissolve, which may be longer than is reasonable for treatment by this method).

Ground water extraction technology is based on two fundamental assumptions [US. EPA, 1989a:3-1]:

(1) a well system can produce ground water flow patterns that will permit the wells to withdraw all of the contaminated ground water from the aquifer,

(2) contaminants will come out of the aquifer with the water. For this study, I will assume that the contaminant of concern is an organic (Carbon Tetra-Chloride [CTET]) which has a high mobility as dissolved species in ground water.

Continuous Pumping

Continuous pumping maintains an inward hydraulic gradient and as such pumping water containing dissolved contaminants can be addressed using standard well mechanics and capture zone theory [Charbeneau and others, 1992:103; US. EPA, 1990:13].

Continuous pumping may be viable in certain instances where the contaminant of interest doesn't sorb highly. Brogan [1991:165-166] conducted a study using the kinetic approach to adsorption which specified ranges of parameters and well combinations which were used in determining when to use pulsed-pumping or continuous pumping. Adams and Virmontes [1993:5-3] concluded that continuous pumping was viable in certain instances as well, primarily when cleanup achievement was evaluated in terms of total remediation

time. Most pump-and-treat systems use continuous pumping. However, a few sites used pulsed-pumping as a technique to increase the efficiency of ground water extraction where contaminants were subject to rate-limited sorption [US. EPA, 1989a:5-1 to 5-2]. The tailing effect of the low solubility, sorbed contaminant in these instances greatly affected the economic and timely removal and renovation of ground water due to their tendency to slowly desorb into the ground water, thus requiring extended periods of pumping and treating to attain desired levels of restoration [US. EPA, 1992:136-137]. Figure 2-2, illustrates tailing during pump-and-treat remediation showing that tailing entails significantly longer pumping times than that predicted by simple equilibrium models:

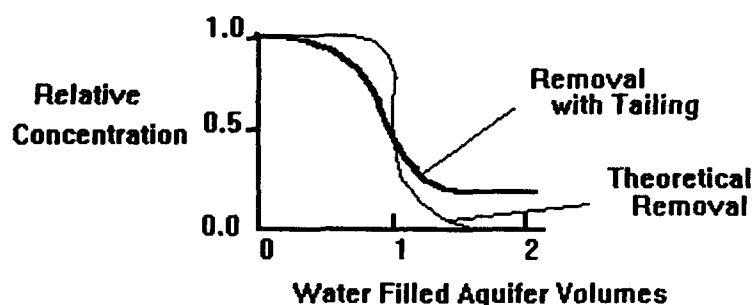


Figure 2.2. Example of Tailing During Pump-and-Treat Remediation
[Schmelling and others, 1992:223; US. EPA, 1990:5]

Another phenomena which occurs after the pumps are turned off is known as 'rebound.' In rebound, contaminant desorbs after the induced gradient returns to equilibrium. This causes contaminant concentrations to rise to a new equilibrium level between that contained in the immobile regions and the mobile regions. The result is an increase in contaminant concentrations after the aquifer was supposedly cleaned-up by

continuous pumping. Figure 2.3, illustrates the rebound aspect with respect to contaminant concentration levels over time:

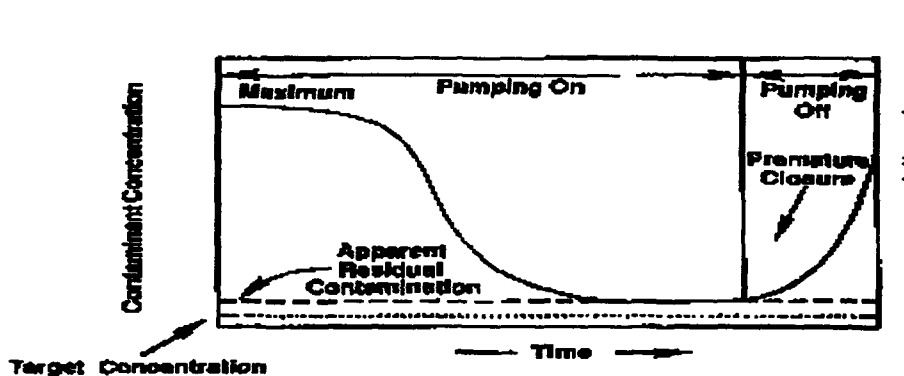


Figure 2.3. Conventional Pump-and-Treat With Rebound
[Gorelick and others, 1993:224]

Pulsed Pumping

An innovation in pump-and-treat technology designed to increase the removal rate for contaminants is pulsed pumping [US. EPA, 1992:137]. The principle behind pulsed pumping is that efficiency in contaminant mass extraction will improve will improve by allowing contaminants located in low permeability zones (such as dead-end pores) to diffuse outward into areas of higher hydraulic conductivity during non-pumping periods [Hall and Johnson, 1992:221]. In this instance the rate of mass removal is primarily controlled by the release of residual contaminants, rather than by the velocity of ground water flow. Thus, the pumping plan should accommodate optimized "rest" periods to allow desorption from the immobile region and terminating when "equilibrium" occurs with the mobile region. Then, when extraction resumes, the minimum volume of ground water can be removed at the maximum possible concentration for the most efficient treatment [US. EPA, 1990:25]. Figure 2.4, illustrates the cyclic nature of pulsed pumping and the removal of rebounded concentrations of residual contaminants:

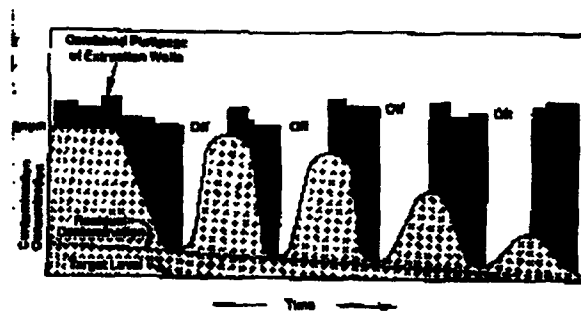


Figure 2.4. Pulsed Pumping of Residuals
[Gorelick and others, 1993:225]

This increased efficiency was seen with a finite element model [Huso, 1989:4-12], and with a kinetic mathematical model [Brogan, 1991:131]. In the former case, using lower pumping rate periods, increased average concentrations of organic species were removed during the "pumping" periods, thus decreasing the total volume of water requiring treatment. In the latter case, optimization of the SUTRA code delineated parameters where pulsed-pumping would be the optimal technology for certain instances using a kinetic sorption model. Similarly, using an analytical code for a first-order, mass-transfer, diffusion model, regions where pulsed pumping would yield better results than continuous pumping were calculated [Adams and Virmontes, 1993:4-19]. In conclusion, an efficient pulsed-pumping alternative (to continuous pumping) should reduce both treatment time and volume pumped (Powers and others, 1991:474).

Summary

The principle measures of operational effectiveness of a remediation design are the general degree of hydrodynamic control exerted and/or the general degree of contaminant cleanup achieved. This effectiveness can be accomplished by examining the spatial uniformity of the control exerted and/or the cleanup level achieved [Gorelick and others,

1993:258-259]. Measures of operational efficiency for selecting remediation procedures are the minimization of total costs required to reach and maintain remediation targets; maximization of contaminant removal per unit volume of ground water pumped and treated; minimization of the total volume of pumped and treated ground water; and time for completion of remediation to a given water-quality level to which to restore the aquifer, as well as the most economical technology available to reach that level.

Pump-and-treat systems are well established as remedial techniques for restoration of ground water. However, many systems have failed to achieve the optimal removal efficiencies due to an incomplete understanding of processes taking place within the soil matrix or overly optimistic assumptions made in the modeling process. In many cases, sorption played a major part in delaying the restoration of ground water quality. Pump-and-treat technology is particularly good in instances where the contaminant of concern does not sorb strongly to the matrix, yet is hydrophobic. In this instance high-pumping at a continuous rate would best achieve removal action, when other alternatives aren't available. However, in the instance of non-equilibrium sorption, where prolonged periods of pumping may occur, innovations such as pulsed-pumping can improve the efficiency of contaminant removal by allowing contaminants to reach equilibrium during rest cycle periods and consequent greater removal of contaminant per volume of water treated [Keely, 1989:9].

A number of authors have voiced concern about the extensive use of pump-and-treat systems in remediation [Cartwright, 1991:64; Haley and others, 1991:119; Hall and Johnson, 1992:215; Bredehoeft, 1994:95]. The basic problem is application of this technology to situations where heterogeneities within the sub-surface interfered with effective pump-and-treat capture of contaminant and sorption effects which extended the

pumping times to uneconomical proportions [US. Congress, OTA, 1989:151]. Some authors have suggested that containment may be the optimal solution in certain situations [Mackay and Cherry, 1989:630; Cartwright, 1991:66; Ross, 1993:92] or reliance on in-situ, bio-remediation [Brubaker and Stroo, 1992:167-168]. Still other authors have sought to optimize the design through use of linear sorption effects while using monte-carlo or numerical models which evaluate uncertainty in hydraulic conductivity [Ahlfeld, 1991:848; Kuo and others, 1992:95,105]. Finally, others have used kinetic approaches towards optimizing the design [Brogan, 1991; Haggerty, 1992]. This thesis seeks to use physical non-equilibrium, diffusion oriented methods to analyze pumping rates and strategies to successfully remediate a hypothetical aquifer.

A further refinement to pump-and-treat, which is beyond the scope of this research is combination of pump-and-treat extraction methods with alternative technologies such as soil flushing, soil venting, chemical enhancements to pump-and-treat or bio-remediation. Discussions concerning these technologies can be found in Ross (1993), Brubaker and Stroo (1992), Bohm (1992), , NGWA (1992), Palmer and Fish (1992), Chambers and others (1990), and Canter and others (1987). Recent research has focused on multi-process, non-equilibrium models [Brusseau and others, 1992a:175; Brusseau (1989b); Lewis and others, 1987:81; Jennings and others, 1984:120; Cameron and Klute, 1977:183], multi-phase contaminant transport (DNAPL's and LNAPL's) [Mayer and Miller, 1990:217] and transport processes through fractured media [Bear and others (1993); Huyakorn and others, 1983b:841]. The fractured media models have great potential for modeling the rapid movements through fractured soils or cracks in confining beds which allow transmissivity to other aquifers. These may warrant further study and development through incorporating physical non-equilibrium diffusion equations for ground water transport problems.

III. SUTRA Model Modification

Introduction

The primary objective of this section is to develop a modification to the USGS **Saturated-Unsaturated Transport (SUTRA)** code which describes contaminant transport by means of advection, dispersion, and physical non-equilibrium sorption (both first- and second-order) in an aquifer. Methods used will extend the work of Goltz and Oxley [1991a], Huso [1989] and Huyakorn, et. al [1983b]. This modification will be validated in Chapter IV through comparison with an analytical code published by Adam's and Viramontes [1993] for a radial, pulsed pumping simulation. The equations, solutions, notation and source code will be based on the expressions of sorption presented in their respective papers as well as in Bear and Verruijt [1987].

This chapter begins with a discussion on the characteristics of SUTRA. Then, the governing equations of ground water flow and contaminant transport will be presented. This equation development will be followed with a discussion of the modifications to SUTRA and end with the iterative solution scheme used to solve for contaminant values in the modification.

SUTRA

General

SUTRA is a computer program which simulates fluid movement and the transport of dissolved substances in a subsurface environment. The model employs a two-dimensional finite-element spatial discretization and integrated finite-difference time-stepping to approximate the governing equations that describe transport in the ground

water [Voss, 1984:3]. Transport of solute is modeled by advection, dispersion and molecular diffusion and assumes equilibrium adsorption on the porous matrix. It provides a choice of linear, 'Freundlich' or 'Langmuir' equilibrium sorption models to accomplish this equilibrium assumption. SUTRA is a public domain code and one of the few which models transport in both the vadose and saturated zones of the sub-surface. Its modular design allows relatively, straight-forward modifications to account for non-equilibrium sorption. This code was primarily intended for two-dimensional simulation of transport of either solute or energy in saturated variable-density systems [Voss, 1984:5]. Models can be extended into three dimensions by assuming a fixed parameter for the aquifer thickness. Brogan has previously modified the code to account for first-order kinetic (chemical) reactions. This thesis will modify the code to account for either first- or second-order (Fickian) diffusion (physical non-equilibrium) within the matrix and its influence on rate-limited sorption behavior of a pump and treat system.

SUTRA Numerical Methods

SUTRA simulation is based on a hybridization of finite-element and integrated-finite-difference methods employed in the framework of the Galerkin method of weighted residuals [Voss, 1984:8]. Standard finite-element approximations are employed only for terms in the balance equations which describe the fluxes of fluid mass, solute mass and energy. All other non-flux terms are approximated with a finite-element mesh version of the integrated-finite-difference method. Time discretization in SUTRA is accomplished through implicit, backward Euler finite differencing.

Physical-Mathematical Basis of SUTRA Simulation

SUTRA simulation combines two physical models, one to simulate the flow of ground water and the second to simulate the movement of a single solute in the ground

water [Voss, 1984:15]. Haggerty [1992:15] modified the code to account for multi-species transport using the first-order, kinetic algorithms developed by Brogan. This was accomplished through simultaneous solution of mass-balance equations at each node and time step for the various component reactions within the matrix. For the modification studied in this thesis, a single-species solute will be studied. A comparison will be made for the effects of first-order and second-order physical non-equilibrium models of sorption/desorption between the mobile and immobile regions assumed within the soil matrix versus that predicted by an LEA model (SUTRA unmodified).

Water Mass Balance Governing Equations

The common starting point in the development of differential equations to describe subsurface ground water movement and the transport of solutes in porous materials is to consider the flux of water mass and solute mass into and out of a fixed elemental volume within the flow domain [Freeze and Cherry, 1979:388]. A conservation of mass statement for such an elemental volume is:

$$\begin{array}{|c|} \hline \text{Rate of} \\ \text{Change} \\ \text{of Mass} \\ \text{in the} \\ \text{Volume} \\ \hline \end{array} = \begin{array}{|c|} \hline \text{Rate of} \\ \text{Mass of} \\ \text{Fluid into} \\ \text{the} \\ \text{Element} \\ \hline \end{array} - \begin{array}{|c|} \hline \text{Rate of} \\ \text{Mass of} \\ \text{Fluid Out} \\ \text{of the} \\ \text{Element} \\ \hline \end{array} + \begin{array}{|c|} \hline \text{Net Rate} \\ \text{of Change} \\ \text{of Fluid Mass} \\ \text{Due to} \\ \text{Reactions} \\ \hline \end{array} \quad (3.1)$$

To translate this statement into mathematical form, consider the volume flux into and out of a small elemental volume in the porous medium, as illustrated in Figure 3.1 below:

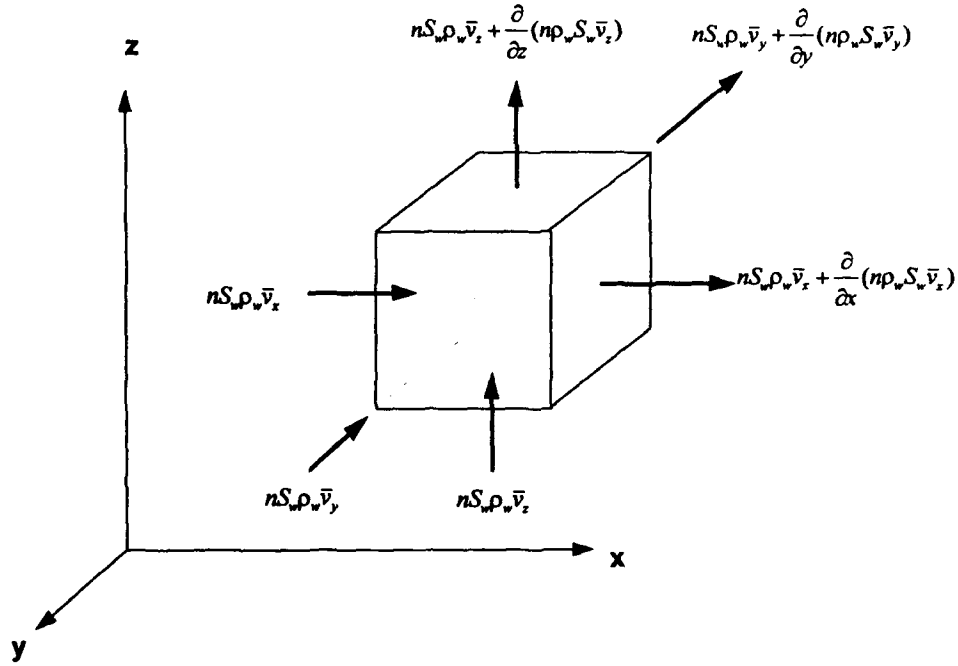


Figure 3.1. Mass Balance in a Cubic Element in Space

where n is the bulk porosity of the soil matrix; S_w is the water saturation index for the soil; ρ_w is the density of water; and \bar{v} is the average fluid velocity. Thus the mass flux, using the previous definitions is $nS_w\rho_w\bar{v}$. Porosity may be found as [Freeze and Cherry, 1979:36; Voss, 1984:19]:

$$n = \frac{\nabla_v}{\nabla_T} \quad (3.2)$$

where ∇_v = the volume of the voids and ∇_T = the total volume of the matrix.

The water saturation index (S_w) for the soil indicates the degree of saturation of the soil matrix. When $S_w = 1$, the void space is completely filled with fluid and is said to be saturated [Voss, 1984:19]. When $S_w < 1$, the void space is only partly water-filled

and is referred to as being unsaturated. In this state, water adheres to the surface of solid grains by surface tension effects and the fluid pressure is less than atmospheric. The water saturation index may be calculated by the following equation:

$$S_w = \frac{V_w}{V_v} \quad (3.3)$$

where V_w is the volume of water within the matrix.

The average fluid velocity (\bar{v}), is the average linear velocity of fluid with respect to the stationary solid matrix within the soil. The average linear velocity does not represent the average velocity of the water particles traveling through the pore spaces, but is a macroscopic term representative of flow through the entire matrix. It may be found from the Darcy's Law equation as:

$$\bar{v} = \frac{q}{n} = -\frac{K}{n} \nabla h = -\left(\frac{k k_r}{n S_w \mu_w}\right)(\nabla p_w - \rho_w g \nabla z) \quad (3.4)$$

where q is the Darcy velocity; K is the hydraulic conductivity of the matrix; k is the solid matrix permeability; k_r is the relative permeability to fluid flow; ρ_w , μ_w , and p_w denote water's density, viscosity and pressure respectively; z denotes elevation; and $(\nabla p_w - \rho_w g \nabla z) = \nabla h$ is the hydraulic gradient (head) for the matrix [Freeze and Cherry, 1979:71; Voss, 1984:25-27; Bear and Verruijt, 1987:40-41].

Hydraulic conductivity (K) is not a fundamental parameter describing flow through the matrix. It is dependent on temperature (which is assumed to be constant in the SUTRA model) and to a lesser extent on concentration. Intrinsic permeability (k) is

used to describe flow in the SUTRA model [Voss, 1984:37] as it is independent of pressure, temperature and concentration (being a function of the medium only [Freeze and Cherry, 1979:27]). The hydraulic conductivity may be found from the following equation:

$$K = \frac{k\gamma}{\mu} \quad (3.5)$$

where k is the intrinsic (specific) permeability; μ is the dynamic viscosity of the fluid; and γ is the weight density (specific weight) of the fluid [Freeze and Cherry, 1979:526].

Using the previous definitions and relationships, we return to the element in [Figure 3.1] to develop an equation for mass balance. SUTRA conducts its flow simulation by calculating how the amount of fluid mass contained within the void spaces of the solid matrix changes with time. The total fluid mass present at any time may be given by:

$$\text{Mass present} = \theta \rho \nabla_T \quad (3.6)$$

where θ is the moisture content of the soil. The volumetric moisture content (θ) of the soil is found by the equation [Freeze and Cherry, 1979:39]:

$$\theta = \frac{\nabla_w}{\nabla_T} = nS_w \quad (3.7)$$

The law of conservation of mass for transient flow in a saturated porous medium requires that the net rate of fluid mass flow into any elemental control volume plus the

net rate of change of fluid mass due to reactions or sources/sinks [Figure 3.1] is equal to the time rate of change of fluid mass storage within the element [Freeze and Cherry, 1979:64]. In a saturated media, $S_w = 1$ so the mass of water in a representative volume is $(n\rho_w)$ and the change in water mass per unit volume of porous media per unit time [Figure 3.1] is given by the equation of continuity for the water [Freeze and Cherry, 1979:531; Bear, 1972:197; Bear and Verruijt, 1987:57]:

$$\frac{\partial(n\rho_w)}{\partial t} = -\nabla(n\rho_w \bar{v}) = n \frac{\partial \rho_w}{\partial t} + \rho_w \frac{\partial n}{\partial t} \quad (3.8)$$

Now, since the total mass of fluid in the element consists of water and dissolved solute, the flow simulation must keep track of the total fluid mass and the solute mass contained at every point in the simulated ground water system. The fluid's total density is the sum of that attributed to water and the contribution from solute dissolved in the water. For solute transport the density is given by [Voss, 1984:18]:

$$\rho = \rho(C) \cong \rho_w + \frac{\partial \rho}{\partial C}(C - C_o) \quad (3.9)$$

where ρ is the fluid density; C is the contaminant aqueous concentration; and ρ_w is the base density of the fluid (usually that of pure water). Using the vectors from Figure 3.1, we apply the conservation of mass principle again, this time to all of the fluid mass in the element [Voss, 1984:33]:

$$\frac{\partial(nS_w\rho)}{\partial t} = -\nabla(nS_w\rho \bar{v}) + Q_p + T \quad (3.10)$$

where Q_p is the fluid mass source (water mass plus dissolved solute mass); and T is the solute mass source (e.g., dissolution of solid matrix or desorption) and

$$nS_w = \frac{V_w}{V_T} = \theta \quad (3.11)$$

Considering the left-hand side of Equation (3.10), the actual amount of total fluid mass contained in the volume depends only on fluid pressure (p) and solute concentration (C) for isothermal flow. The change in total mass of the fluid with time, assuming the volume is constant is [Voss, 1984:22; Bear and Verruijt, 1987:57]:

$$V_T \frac{\partial(nS_w \rho)}{\partial t} = \frac{\partial}{\partial t}[(\theta \rho) V_T] = V_T \left[\frac{\partial(\theta \rho)}{\partial p} \frac{\partial p}{\partial t} + \frac{\partial(\theta \rho)}{\partial C} \frac{\partial C}{\partial t} \right] \quad (3.12)$$

Saturation (S_w) depends only on fluid pressure and porosity (n) does not depend on concentration. Since S_w is a function only of p :

$$\frac{\partial(\theta \rho)}{\partial p} = \frac{\partial(nS_w \rho)}{\partial p} = S_w \frac{\partial(n \rho)}{\partial p} + n \rho \frac{\partial S_w}{\partial p} \quad (3.13)$$

and

$$\frac{\partial(\theta \rho)}{\partial C} = \frac{\partial(nS_w \rho)}{\partial C} = nS_w \frac{\partial \rho}{\partial C} \quad (3.14)$$

Substituting Equations (3.13) and (3.14) into Equation (3.12) we obtain an expression for the rate of fluid mass stored in the representative elemental volume:

$$\frac{\partial[\nabla_T(nS_w\rho)]}{\partial t} = \nabla_T \left[(S_w \frac{\partial(n\rho)}{\partial p} + n\rho \frac{\partial S_w}{\partial p}) \frac{\partial p}{\partial t} + nS_w \frac{\partial \rho}{\partial C} \frac{\partial C}{\partial t} \right] \quad (3.15)$$

Beginning with Equation (3.8), I will now discuss the effects of vertical compressibility on the deformable (consolidating) porous medium. The specific mass storativity (S_{op}) is the mass of fluid released (or added) to a unit volume of porous medium per unit decline (or increase) in pressure [Bear, 1972:204]. It is related to pressure changes by:

$$\frac{\partial p}{\partial t} S_{op} = -\rho[\beta n + \alpha'(1-n)] \frac{\partial p}{\partial t} = \rho \nabla \bar{v} \quad (3.16)$$

where β is the coefficient of compressibility of water; and α' is the soil coefficient of compressibility. Aquifer storativity under fully saturated conditions is related to the factor, $\partial(n\rho)/\partial p$ as follows [Voss, 1984:23]:

$$\frac{\partial(n\rho)}{\partial p} = \rho S_{op} \quad (3.17)$$

Expanding Equation (3.17) we obtain the relationship [Bear, 1972:205; Voss, 1984:23]:

$$\frac{\partial(n\rho)}{\partial p} = \rho S_{op} = \rho \frac{\partial n}{\partial p} + n \frac{\partial \rho}{\partial p} \quad (3.18)$$

Substituting Equation (3.18) into Equation (3.15) and then substituting the resultant equation into Equation (3.10), in addition to using Equation (3.4) for the Darcy velocity we obtain the more exact form of the fluid mass equation which is used in SUTRA (ignoring T) [Voss, 1984:34; Bear and Verruijt, 1987:63]:

$$Q_p = \nabla \left[\left(\frac{k k_r \rho}{\mu} \right) (\nabla p - \rho g \nabla z) \right] + (S_w \rho S_{0p} + n \rho \frac{\partial S_w}{\partial p}) \frac{\partial p}{\partial t} + (n S_w \frac{\partial \rho}{\partial C}) \quad (3.19)$$

Contaminant Transport Equation

SUTRA models solute mass transport through use of an advection-diffusion equation, with the addition of a dispersion term to approximate the effects of mixing of waters with different concentrations moving both faster and slower than the average velocity (\bar{v}) [Voss, 1984:38]. This equation represents the total mass of a single species of adsorbent by summing separate equations for the mass balance of that stored in solution and that stored on the solid grains (adsorbate). The derivation of the equations for contaminant mass balance follows the same pattern as that done above for the ground water which culminated in Equation (3.19). The separate balances for a single species stored in solution (solute and on the solid grains (adsorbate), are expressed, respectively, as follows [Voss, 1984:40]:

$$\frac{\partial(\theta \rho C)}{\partial t} = -f - \nabla(\theta \rho \bar{v} C) + \nabla[\theta \rho (D + D_d^*) \nabla C] + \theta \rho \Gamma_w + Q_p C^* \quad (3.20)$$

and

$$\frac{\partial[(1-n)\rho_s F]}{\partial t} = f + (1-n)\rho_s \Gamma_s \quad (3.21)$$

where F is the mass of solute adsorbed on the solid per unit mass of solid.

These in turn are coupled additively to yield the general form of the SUTRA integrated equation used for total species mass balance [Bear and Verruijt, 1987:170; Voss, 1984:42]:

$$\frac{\partial(\theta\rho C)}{\partial t} = -\nabla[S_w\rho(q_{c,total})] - \frac{\partial\theta_s\rho_s F}{\partial t} + \theta_s\rho_s\Gamma_s + \theta\rho\Gamma + Q_p C^* \quad (3.22)$$

where θ_s is the solids volumetric fraction, ρ_s is the solids density, Γ_s is the rate of production of the solute per unit mass of solid, and $Q_p C^*$ is the dissolved species mass added by a fluid source with concentration C^* .

The last term in Equation (3.22) is represented by some as two separate terms, and can be found by the equation [Bear and Verruijt, 1987:170]:

$$Q_p C^* = -PC + R_Q C_R \quad (3.23)$$

where P is the rate of water withdrawn at a pumping well, R_Q is the rate of water added at an injection well, and C_R is the solute concentration in water injected into the medium. The term θ_s may be found by the equation:

$$\theta_s = \frac{V_s}{V_T} = 1 - n \quad (3.24)$$

Advection, Dispersion and Diffusion

There are four components taken into account in the construction of the solute mass balance equation [Equation (3.22)] [Bear and Verruijt, 1987:168]. The first is the quantity of the pollutant entering and leaving a control volume around a considered point by advection, dispersion and diffusion. The total flux portion of Equation (3.22) is represented by :

$$q_{c,total} = Cq - qD\nabla C - qD_d^*\nabla C \quad (3.25)$$

where D is the coefficient of mechanical dispersion; D_d^* is the coefficient of molecular diffusion in a porous medium.

Advection is caused by motion of the fluid into the control volume [Freeze and Cherry, 1987:389]. This is represented by the first term in Equation (3.25), where the net rate of solute inflow is $-\nabla(\theta\rho\bar{v})$. Mechanical dispersion is mixing that occurs as a consequence of local variations in velocity around some mean velocity flow [Domenico and Schwartz, 1990:369]. The coefficient of mechanical dispersion (D) is the result of the motion of the water in the pore spaces, due to differing velocities which the water will travel in the pore space (channels), differences in surface area and roughness relative to the volume of water in individual pore channels and tortuosity related to the branching and inter-fingering of pore channels [Freeze and Cherry, 1979:75-76]. A number of authors have discussed methods of calculating the coefficient of dispersion (D) [Freeze and Cherry, 1979:389-390; Bear and Verruijt, 1987:161-164]. SUTRA [Voss, 1984:48-50] uses a 2×2 matrix to compute mechanical dispersion in the manner suggested by Bear and Verruijt. The flux associated with molecular diffusion (D_d^*) at the microscopic level originates because of diffusion related to mixing caused by random molecular motions caused by the thermal kinetic energy of the solute [Domenico and Schwartz, 1990:367]. Its effects are represented by the third term in Equation (3.25). Values for the molecular diffusion coefficient can be calculated by the empirical methods of Bear and Verruijt [1987:164-165] or by some more general empirical approaches to approximate an effective diffusion coefficient (D_d') in place of the molecular diffusion coefficient (D_d^*) along with some tabular values for ionic diffusion coefficients.

Equilibrium Sorption Isotherms

The next term of Equation (3.22) is that representing pollutant leaving the fluid phase through adsorption through the water-solid interface as a result of chemical or electrical reactions. This is represented by the volumetric adsorbate term (f) in Equations (3.20) and (3.21), which denote the quantity of solute that leaves the water by such mechanisms, per unit volume of porous medium, per unit time [Bear and Verruijt, 1984:168]. This represents adsorption. Within SUTRA, the volumetric adsorbate source term (f) is represented by equilibrium isotherms, which relate the rate of transfer between the mobile and immobile zones per those found in Table 2.1. In general these isotherms take the form:

$$\frac{\partial F}{\partial t} = (Const.) \frac{\partial C}{\partial t} \quad (3.26)$$

which reduces the number of unknowns in Equation (3.22) from two unknowns (F and C) to one unknown (C). The three isotherms used by SUTRA are either: linear sorption, Freundlich equilibrium sorption, or Langmuir equilibrium sorption. Should adsorption not be a factor, the code makes provision to zero this term out. Later, we will discuss the methods used to represent this term with a second-order diffusion equation.

Sources and Sinks Within the Liquid Phase

Sources and sinks of the solute are expressed by the third and fourth terms in Equation (3.22), $\theta_s \rho_s \Gamma_s + \theta \rho \Gamma$. These result from various processes, e.g., chemical reactions among components within the liquid, radioactive decay and bio-degradation [Bear and Verruijt, 1987:173; Voss, 1984:46]. Bear and Verruijt [1987:173] provide a

generic discussion of sink terms and decay constants, as do Domenico and Schwartz [1990:475-477].

Solute Mass Additions

The final term of Equation (3.22) is that attributed to solute which may be added by injecting polluted water or through removal of mass through pumping ($Q_p C^*$). This term accounts for additions in mass due to recharge of the aquifer by contaminated water by a given concentration, or removal, through pumping of contaminated water from the medium. This addition, serves to balance the equations used in tracking the mass balance throughout the system.

Implementing Non-Equilibrium Sorption in SUTRA

General

As discussed in Chapter II, physical non-equilibrium models are commonly based on a two-zone description of a porous medium, with transport in the mobile zone governed by the advective-dispersive equation (Equation [2.3]) with the retardation factor adjusted, as in Equation (2.9), to account for a mobile zone sorption [Harmon and others, 1989:409-410]. The first-order rate model (Equation [2.11]) assumes that the immobile zone is completely mixed and that mass transfer across the mobile-immobile interface is described by a first-order expression. A second-order rate model (Equations [2.13] and [2.14]) is one which considers the transfer of solute within the immobile region as being diffusion driven, using Fick's law of diffusion. SUTRA's algorithms are structured for local equilibrium conditions. However, it does accommodate non-equilibrium sorption models, through use of kinetic sorption coefficients to formulate a value for a specific sorption rate (f_s), which in turn can be used in calculation for a value of the volumetric adsorbate source, (f) for use in Equations (3.20) and (3.21). Traditional approaches

couple Equations (3.20) and (3.21). Equations (2.13), (2.14) and (3.22) are then solved simultaneously for the spherical diffusion model to account for three-dimensional transport in the soil matrix. Bibby [1981:1075-1076] demonstrated use of the three-dimensional equations above, while analytically solving for one-dimensional diffusion within a spherical block for Equation (2.17). This implementation requires storage of previous immobile zone solutions. In contrast, Huyakorn, et. al [1983b:842] used a finite-element solution of the immobile zone equation [Equation (2.16)] in a fractured media model. The solution flexibility and smaller storage requirements of this method favor the latter approach. Therefore, transport in the spherical matrix block, which represents immobile zones, will be approximated by a one-dimensional, finite-element solution that is sequentially coupled with the two-dimensional approximation of the mobile zone via leakage flux terms.

The conceptual matrix models used in this thesis effort are shown graphically in Figures 3.2 and 3.3, below:

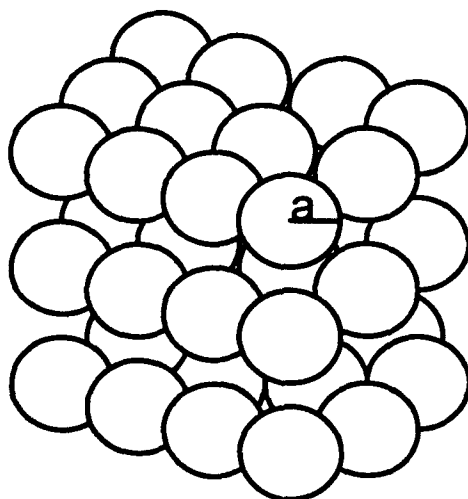


Figure 3.2. Dual Porosity Media-Spherical Blocks
[Huyakorn and others, 1983b:843]

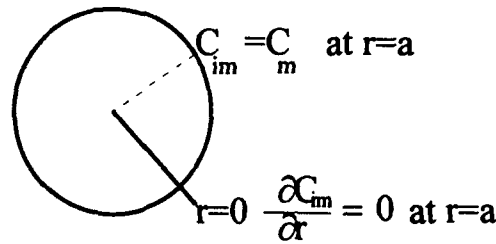


Figure 3.3. Discretization of Spherical Immobile Region
[Huyakorn and others, 1983b:843]

Huyakorn [1983b:843] solved for the concentration values within the spherical immobile region represented by Figure 3.3 by the equation:

$$\frac{\partial C_{im}}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{im}}{\partial r} \right) \quad (3.27)$$

and the concentration flux at the boundary of the layers of the immobile and mobile zones of Figure 3.2 by:

$$f = - \frac{3D_e}{a} \frac{\partial C_{im}}{\partial r} \bigg|_{r=a} \quad (3.28)$$

This expression simply relates the mass flux of contaminant flowing into or out of the immobile zone to the spatial gradient at the zone's perimeter.

The overall solution procedure for the non-equilibrium equations, either Equation (2.11) for first-order or Equation (2.13) for second order, follows an iterative solution scheme set forth by Huyakorn, et al [1983b:846] for fractured media flow and Miller and Rødoideau [1993:2229] for the operator-splitting technique. Using the split-operator approach, the governing equations are separated into transport (for the mobile zone) and reaction operators (diffusion equations for the immobile zone) and solved sequentially. This splitting allows the separation of the short-time scale process (mobile zone) from the

long-time scale process (immobile). Operator splitting leads to smaller systems of equations, which can be solved faster than coupling the diffusion equation into Equation (3.22). As outlined above, my approach will entail solving Equation (2.10) for first order or Equations (3.27) and (3.28) for second-order diffusion, and finding the fluxes using the split operator approach. The results will then be sequentially used to solve Equation (3.20) at each time step, for the mobile region concentration at the respective nodes. Miller and Rabideau [1993:2229] further discussed the numerical stability and computational advantages of this method in greater detail.

First Order, Non-Equilibrium Assumption

Assuming that $\Gamma_s = 0$ simplifies Equation (3.21) and the remaining term, f in the equation is the rate of solute transfer from the matrix block to the mobile zone per unit volume of the matrix block. Van Genuchten and Wierenga [1976:474] established a first-order relationship for the immobile zone concentration, which is given by Equation (2.7). The concentration within the immobile region is assumed to be a volumetric averaged constant and is equal to the concentration at the boundary with the mobile zone. The first order rate constant, for layered, spherical aggregates, corresponds to the following equation [Van Genuchten, 1985:522; Goltz, 1986a:56]:

$$\alpha = \frac{22.68 D_e \theta_{im}}{a^2} \quad (3.29)$$

where D_e is the effective diffusion coefficient, θ_{im} is the immobile zone porosity and a is the layered half width for the immobile region (Equation [3.27] is the same if the spherical immobile region radius $[a]$ is known as well). This relationship is used, in turn, to solve Equation (3.21), where the resulting equation:

$$\frac{\partial[(1-n)\rho_s F]}{\partial t} = f = \alpha(C_m - C_{im}) \quad (3.30)$$

is used to solve the SUTRA integrated equation for total species mass balance (Equation[3.22]).

Second- Order, Non-Equilibrium Assumption

Instead of using the LEA to further simplify the solution to equations (3.20) and (3.21), an expression for f in Equation (3.21) may be found by solving the one-dimensional diffusion equation (Equation [2.13]) for C_a using the following boundary conditions, from Figure 3.3:

$$C_a(a) = C_m \quad (3.31)$$

and

$$\left. \frac{\partial C_a}{\partial t} \right|_{r=0} = 0 \quad (3.32)$$

The non-equilibrium transport problem, Equation (3.20), is solved through iterative solution of Equations (3.27) and (2.28) using the split operator technique, to determine the mass flux from the immobile zone into the mobile zone, using the boundary conditions of Equations (3.31) and (3.32).

Iterative Solution Scheme

For second-order calculations, at the initial time step, the mobile and immobile concentrations are assumed to be equal (at the boundary of the spheres). Thus $f = 0$ at all points. Then, using a modified form of SUTRA, Equation (3.21) is solved for the concentration of the mobile zone at C_m^{k+1} (superscript represents time) iteration at each node. The C_m^{k+1} values (where C_m is the mobile zone concentration) at each node then serve as a boundary condition [Equation (3.31)] for the immobile zone concentration (C_{im}^k) calculation at each node using Equation (3.28). The mobile/immobile zone interface iteration can be summarized by the following equation:

$$C_a(a) = C_m^{k+1} \quad (3.32)$$

Then the immobile zone concentrations within the spherical-immobile regions are calculated using a one-dimensional finite element code [Pepper and Heinrich, 1992:226] with C_a^k as an initial condition estimate for the calculation of a revised value estimator for C_a^{k+1} . Finally, the flux into or out of the spherical immobile region (f) is computed using Equation (3.28) and used as a source term (f) in the mobile zone calculation of Equation (3.20). For the next cycle, the improved estimate for the C_m^{k+1} values at each node are used to update the concentration values for the immobile zones in step two above, and conduct another series of one-dimensional Galerkin solutions in the same manner as before.

IV. Analysis and Evaluation of Results

Introduction

This chapter presents results using modifications made to the SUTRA code based on the analysis developed in Chapter III. First, model verification is asserted by validating the modified SUTRA code with an analytical code developed by Adams and Virmontes (1993), in a one-dimensional (1-D), radial pumping test, for both first- and second-order diffusion effects that emulate rate-limited sorption and desorption. Then, a hypothetical two-dimensional (2-D), contaminated, sandy aquifer was developed using realistic parameters to facilitate the remainder of the analysis. The discussion of aquifer parameters included analysis of input parameters for placement within the non-equilibrium regime. Repeated simulations on this hypothetical aquifer provided a means of finding discrepancies between the first- and second-order, rate-limited model predictions of mobile zone concentrations and cleanup times. These simulations also provided insight into the effectiveness of pulsed-pumping as a remediation strategy when a pump and treat system is considered.

Validation of Model Modifications

Introduction

The basis for model verification was to compare this model with an existing model formulated using the same sorption/desorption assumptions and through incorporating changes which had been separately validated by their originators. In Chapter II a review of the literature related to modeling sorbing solute transport was conducted. The review

focused on models incorporating either equilibrium or rate-limited sorption, with the rate limitation described by either a first-order equation, or by Fickian diffusion in immobile regions of an aquifer.

The literature review discussed models presented by various researchers which met the above criteria. For purpose of validation comparison, the analytical model presented by Adams and Virmontes [1993] was used. Their model compared favorably with another analytical model [Goltz and Oxley, 1991a] and a numerical model [Huso, 1989]. The Adams and Virmontes model solved a similar sorption/desorption equation set to that used in SUTRA, for a radial pumping simulation, for both first- and second- order cases. The situation they simulated assumed a non-sorbing solute (retardation coefficient[R] of 1.0) in a radial flow field. The simplified geometry allowed the use of 1-D equations which yielded an analytical solution. Another unique feature of the Adams and Virmontes [1993:4-25] code was that it allowed specification of arbitrary initial conditions and pulsed-pumping within the aquifer.

The separate portions of code combined for the modified SUTRA have been validated individually. One reason for the choice of SUTRA was its history of validation [Voss, 1984:180]; peer review [Van der Heijde and Elnawawy; 1993:C.4-2-1]; and application to field problems by many users [Kolodny, 1989:147; Van der Heijde and Elnawawy, 1993:C.4-2-1]. The primary modification to the SUTRA code as outlined in Chapter III, was modeling of the immobile region through use of a 1-D finite element code. The immobile region code was based on a method developed by Pepper and Heinrich [1992:226] and the method had been validated separately against analytical solutions to diffusion problems. Huyakorn et al [1983b:847] validated the approach used

in the transport portion of the code through use of a dual-porosity model in solution of 2-D problems involving transport in fracture and radial spherical matrix diffusion. Finally, split operator methods used to solve the transport and reaction equations separately at each time step have been shown to converge and numerical error minimized when the size of the time step chosen was small compared to the time scale of the transport or reaction process under consideration [Miller and Rabideau, 1993:2233-2234]. The SUTRA modification used five (5) time steps in the spherical diffusion regime for every time step taken within the transport or reaction iterations. In all cases, the transport, reactive and diffusive module components maintained Courant numbers less than one ($C_r = v_x \Delta x / \Delta t < 1$) and mesh Peclet numbers less than two ($P_e = v_x \Delta x / D_x < 2$) throughout the radial simulation, where Δx is the macroscopic grid spacing and Δt is the time step. This was particularly important as numerical instabilities are minimized and molecular diffusion effects are ascendant when $P_e < 2$ and $Cr < 1$ [Goltz and Roberts, 1986b:89; Anderson and Woessner, 1992:327].

Radial Test Input Parameters

In this simulation, model comparisons were made between pulsed pumped and continuous pumped aquifers for both first-order equations and second-order diffusion within the immobile zones. The pulsed-pump simulation for the first-order simulation consisted of cycling the pump on and off at 60-day intervals for a total duration of 120-days. There was no initial hydraulic gradient in the aquifer, hence heads were everywhere equal. The pumping rate was constant throughout the pumping period. The initial mobile and immobile contaminant concentration distributions were set at 1.0 (dimensionless) throughout the 56-meter diameter site of contamination and 0.0 for both mobile and immobile regions outside the site boundaries. A radial mesh was generated by SUTRA

using a plume radius (r_p) of 28-meters, with mesh points generated at 0.07 meter intervals near the pump, increasing to 0.7 meter intervals at the outer portion of the domain.

Appendix A lists the other input parameters used for this simulation.

Results of Validation

The first-order diffusion modification to SUTRA showed good agreement throughout the simulation. Similarly, the second-order diffusion modification compared favorably at the initial time steps for concentration, as shown in Table 4.1 below.

However, the second-order model showed significantly more extraction taking place (and consequently less retardation) at larger simulation times than the analytical model.

This difference is attributed to a number of factors:

a. The difficulty in simulating a 1-D flow field uniformly across the SUTRA finite element grid to match the analytical 1-D solution.

b. Instability in the Laplace transforms and Green's functions of the analytical model. As a result of these instabilities, the analytical code was unable to compute a solution during the pump-off cycle for the second-order model.

c. SUTRA's boundary condition routines did not allow for a complete representation of the conditions used at the outer boundary for the analytical code.

Despite the divergence of the second-order model solution at larger values for time, its solution was qualitatively in agreement with the analytical model. The SUTRA modification was considered valid for employment in modeling contaminant transport in

the soil matrix due to its similar form, behavior and comparable results to the first-order solution for pulsed pumping.

TABLE 4.1
COMPARISON OF FIRST- AND SECOND-ORDER NODES TO ANALYTICAL
MODEL
(VALUES ARE CONCENTRATION AT THE PUMPING WELL)

Day	1st-Order Analytical Code	1st-Order SUTRA Modified	2nd-Order Analytical Code	2nd-Order SUTRA Modified
24	0.999	0.999	0.999	0.997
60	0.621	0.655	0.729	0.524
120	0.620	0.673	N/A	N/A

Model Aquifer Parameters

General

A search of the literature was conducted to determine parameters which were representative of "reality" (in the absence of field data) for input into the model simulation. Orientation was on the well known Borden experiment [Roberts and others, 1986; Mackay and others, 1986]. This case was chosen because it provided controlled data, had been studied at length and published and cross-referenced parameters were available. Additionally, this case would enable achievement of all of the assumptions made in Chapter I. For ease of solution, a homogeneous aquifer simplification was made, even though it has been postulated that Borden's retardation behavior was due more to

heterogeneity in the matrix than rate-limited sorption [Burr and others, 1994:813]. Pulsed and continuous pumping at a constant rate when the pump was on, were employed at the injection point to simulate remediation of the mobile water within the aquifer to a hypothetical clean-up standard. The plume radius (r_p) was defined as the radius at which the concentration was 1% of the cleanup standard (5×10^{-11} g/l). Appendix B, summarizes geophysical factors which were used in the simulations.

Validation of Non-Equilibrium Regime

Many authors have postulated regimes where non-equilibrium was considered ascendant in so far as its effects on dispersion. Brusseau and Rao [1989d:43] stated that in regions where the Peclet number was less than 20 ($P_e < 20$), dispersion would have significant, if not dominant effects; whereas non-equilibrium effects would be dominant at higher Peclet number regimes. This translates to non-equilibrium effects near the pumping well and dispersive effects further away from the pumping well. Computation of Peclet numbers for various radii from the injection point verified that P_e numbers were less than 20 for all points within the plume radius from the proposed extraction point and lower for outer points ($P_e < 10$) within the mesh for all immobile zone radii (a), pumping rates (Q_w), and diffusion coefficients (D_e) in Appendix B. Simulation in these regimes attempted to capture non-equilibrium effects at the lead portion of their applicability. Unfortunately, this low Peclet number regime made the hydrodynamic dispersion effects difficult to distinguish from non-equilibrium effects.

Finite Element Mesh

As outlined above, some authors had specified mesh selection using the equations below to eliminate overshooting and reduce inaccuracy [Goltz and Roberts, 1986b:89]:

$$\frac{v_m \Delta x}{D_e} \leq 2 \quad (4.1)$$

$$\frac{v_m \Delta t}{\Delta x} \leq 2 \quad (4.2)$$

Anderson and Woessner [1992:327] further refine these criteria by stating that the grid should be designed so that:

$$\Delta l < 4\alpha_L \quad (4.3)$$

$$\Delta t < \frac{\Delta l}{v} \quad (4.4)$$

The hypothetical aquifer's finite-element mesh was designed by using Equations (4.1) through (4.4), to specify the maximum grid element size (Δl) and time increment (Δt) which would maintain the $P_e < 2$ in the macropores for the plume. Therefore, a uniform finite element mesh 28-meters in length and 15-meters in width was generated by SUTRA for model formulation. A maximum Δt value of 1.0 day was used, although smaller intervals (0.1 - 0.5 day) were preferable and used during pumping periods for second-order simulations on selected intervals and 0.01 day for first-order simulations throughout to improve accuracy and stability. The contaminant plume was injected at a point four meters in from the left boundary and centered laterally. The primary intention for selecting the size of the mesh was the desire to reduce computational time required for solution of the second-order modification. The ratio of longitudinal to transverse dispersivity (12:1) resulted in a distinctly elongated plume in the direction of ground water flow, which is a characteristic feature consistent with field observations often observed at ground water contamination sites [Palmer and Johnson, 1989:9]. Figure 4.1 illustrates the

rectangular mesh generated and its associated boundary conditions for the contaminant plume:

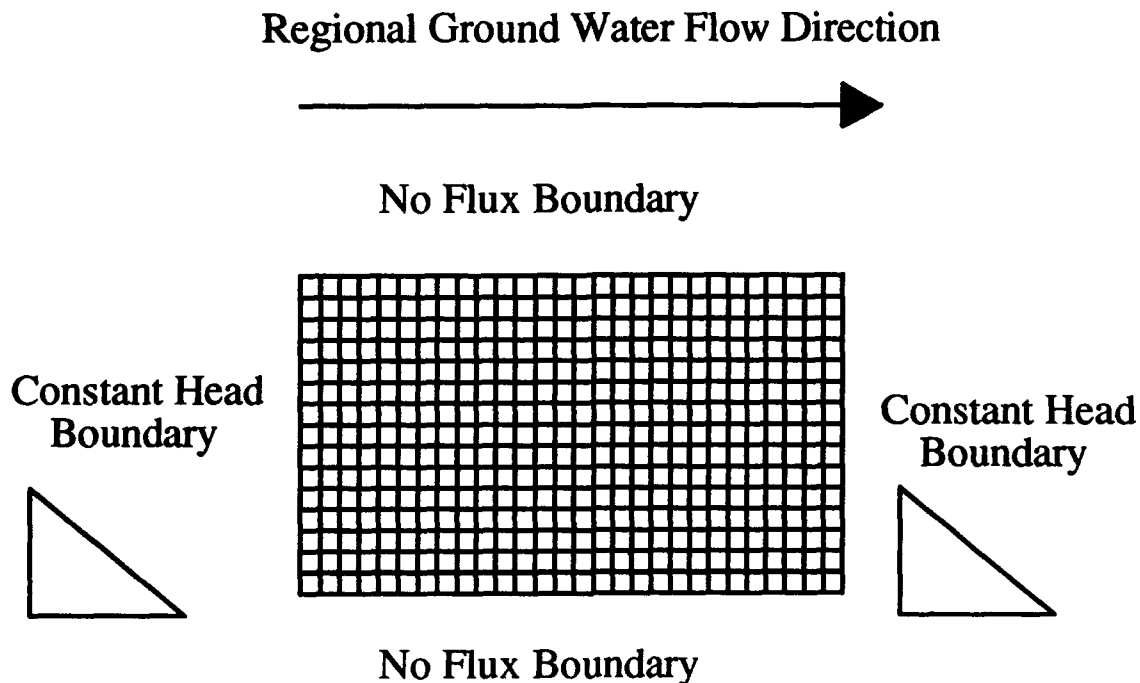


Figure 4.1. Finite Element Mesh and 2-D Boundary Conditions for Hypothetical Model

Immobile Region Mesh

Chapter III discussed modeling of the immobile region using a finite element code developed by Pepper and Hienrich [1992]. The finite element mesh for the sphere used to simulate the layered immobile region was manually generated by assuming the region from the center of the sphere to the outside region would consist of 31 elements. Each node of the immobile zone finite element mesh diffuses through its boundaries in the direction of the concentration gradient. Originally the plume was generated using a non-sorbing solute and the spheres had not "charged up" with contaminant. The first time step of the initial pumping simulation "charged" the immobile zone by setting the concentration within all spherical mesh elements equal to the initial mobile zone concentration. Thereafter, the

immobile zone discharged by means of a flux toward the mobile zone, thereby increasing the mobile zone concentration (causing tailing and rebound) and decreasing the immobile zones concentration toward an equilibrium state. At equilibrium all nodes within the immobile zone achieved a steady state concentration and the flux there from was necessarily very small (eventually approaching zero). The finite-element mesh generated for the immobile zone was fine at either end of the concentration profile (center and exterior) and coarser in the center of the profile where gradients were not as large. Appendix C summarizes the finite-element radii for the layered half-widths for the Borden immobile regions studied.

Boundary Conditions

Boundary conditions for ground water flow consisted of specified head boundaries on all sides of the model, as depicted in Figure 4.1 above. Values of head were fixed to maintain a constant hydraulic gradient of 0.005 in the aquifer. At the right and left edges of the model, as indicated in Figure 4.1, the regional ground water velocity (0.079 meters/day [28.8 meters/year]) was represented by a pressure value, with the high pressure on the left and a low pressure value on the right edge of the mesh. No flux boundaries were established at the top and bottom edges of the model respectively. In the absence of pumping, these boundary conditions simulated spatially constant and steady ground water flow from the left to the right through the aquifer.

Boundary conditions for contaminant transport consisted of constant zero concentrations specified at all model boundaries. All water entering the aquifer from the boundaries was assumed contaminant free. Longitudinal and transverse dispersivity parameters were chosen in an iterative manner, vice use of the Borden values, to ensure

that the gradient did not migrate near the previously selected mesh boundaries. However, the longitudinal-to-transverse dispersivity ratio (12:1) was within the range of values found within the literature as being representative of Borden (2.5-20:1). Selection of this operating constraint whereby plume migration was kept within the mesh boundaries negated the need for any plume contaminant controls during pump-off cycles of the remediation design.

Initial Contaminant Plume

Steady state ground water flow and transient solute transport were simulated. Contaminant was simulated by injection of CTET into the matrix at the rate of $5 \text{ m}^3/\text{day}$, with a concentration of $5.0 \text{ } \mu\text{g/l}$, for a period of 100-days. While the initial concentration appeared to be small and was equivalent to the EPA drinking water standard, this was chosen to allow relatively rapid "clean-up" of the hypothetical aquifer. Larger concentrations should take longer to remediate, but would display the same general effect of the lower concentration case, but over a longer time scale. Upon completion of pumping of contaminant into the matrix, the injection well was turned off for an additional period of 365-days. Advective/dispersive forces in conjunction with the pressure gradient (simulating clean water flow into the matrix) continued to act on the plume, spreading it through the simulated mesh. The contaminant plume is shown in Figure 4.2. Solute concentrations in Figure 4.2 range from 0 to $76 \text{ } \mu\text{g/l}$. The elliptical shape and symmetry of the plume resulted from the hypothetical conditions of the contaminant source, homogeneous flow and transport in the simplified aquifer system. This plume served as a tool for approximating and analyzing remediation strategies incorporating rate-limited sorption for the remainder of this thesis.

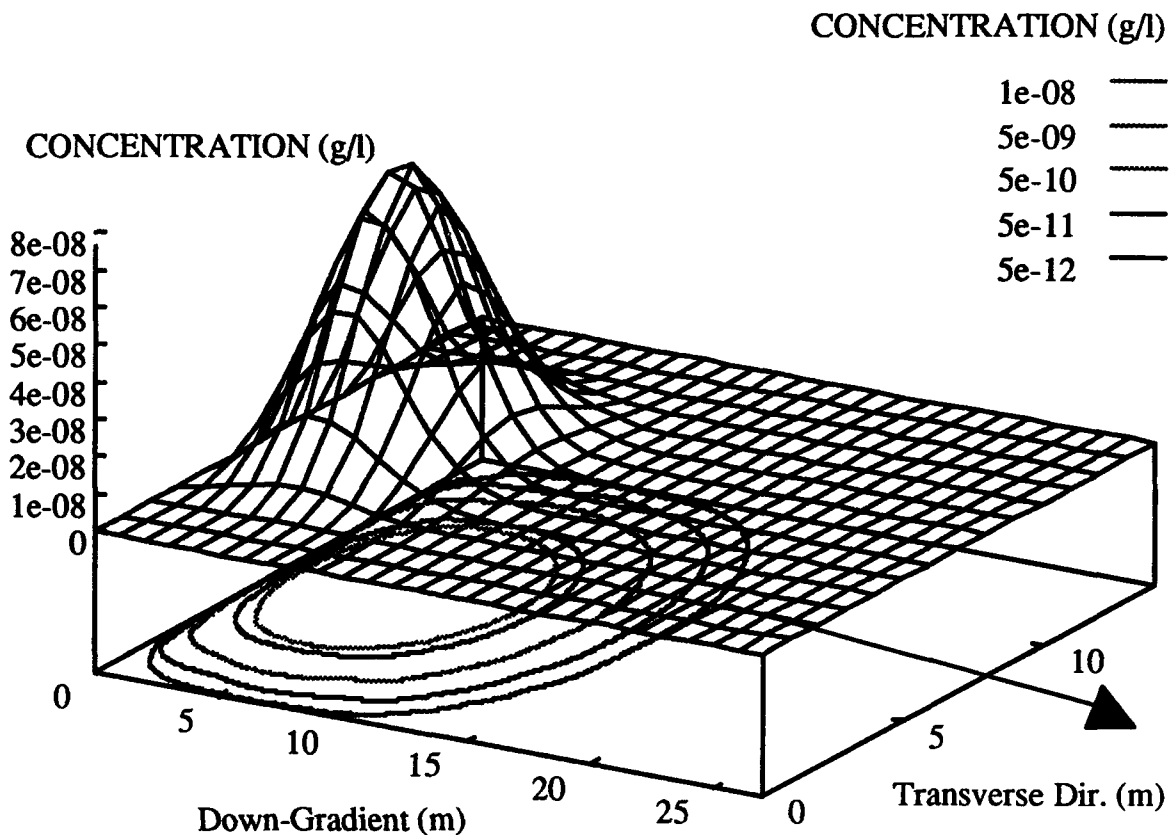


Figure 4.2. Initial Contaminant Plume for Hypothetical 2-D Ground Water Model

Aquifer Remediation

General

The remediation system consisted of a single ground water extraction well, located at the injection point previously used and within the area of the plume. Pumping was continuous at a constant rate during the pump-on cycle, with alternative pump-off (rest) cycles until the aquifer was fully remediated. The pumping well had a dual role, in that it not only extracted the contaminant mass from the aquifer, but also functioned as a monitoring well for cleanup standard achievement by mobile zone concentrations. This dual role is common in typical field cases. Prior to performing the simulations, it was necessary to define how complete remediation of the aquifer was to be determined.

Pulsed pumping and rest period criteria also required definition. After these criteria were specified, measures of optimality or efficiency were defined.

Criteria to Define Aquifer Cleanup

Water quality or drinking water standards are sometimes used as the regulatory criteria to define cleanup of an aquifer [Brogan, 1991:80]. A rough standard for drinking water has been previously defined as 5.0 $\mu\text{g/l}$. As the initial concentration was arbitrarily low, 1% of this value (0.05 $\mu\text{g/l}$) was chosen as the cleanup standard for this simulation. It was necessary for "rebound" in solute concentrations from rate-limited sorption effects to remain below this criterion after pumping was stopped.

LEA Model

For unmodified SUTRA using equilibrium assumptions, aquifer cleanup could be achieved when the solute concentration at all nodes in the model fell below 0.05 $\mu\text{g/l}$. The output files from SUTRA facilitate observation of the concentration at all nodes within the mesh. Observation was made of the entire mesh to ensure complete capture of the plume for the pumping rates selected and it was found that during pumping the highest concentration was at the pumping well (due to inward radial flow). When the cleanup criterion was met and no rebound was observed for rate-limited sorption, the remediation was considered complete, pumping was stopped and the simulation ended. Due to the equilibrium assumption, the solute concentration would continue to monotonically decrease with an equilibrium model (due to lack of rebound and continued advection or extraction), it was impossible for the solute concentration to rebound following the termination of pumping. It was therefore unnecessary to verify that the equilibrium simulations concentrations remain below the cleanup criteria after cleanup is "achieved".

For purpose of analysis a breakthrough comparison of the unmodified SUTRA was expected to show earlier breakthrough and achievement of the cleanup standard, prior to rate-limited sorption models, as well as a monotone decrease with pumping. Continued pumping beyond the cleanup standard was moot, in this case, as only "clean" water would be extracted.

Non-Equilibrium Model

When simulating non-equilibrium conditions, local equilibrium between the sorbed and mobile phase concentrations was not assumed. Although mobile (extracted) phase concentrations often fell below the cleanup criteria, contaminant would typically reappear through rebound and the breakthrough curve would exhibit tailing behavior as it asymptotically sought an equilibrium level. Thus for both pulsed and continuous pumping situations, cleanup was achieved when the rebound of the contaminant no longer exceeded the cleanup standard. The standard of 0.05 $\mu\text{g/l}$ (1% of drinking water standard) was used to ensure that rebound effects from desorbing solute did not exceed the primary drinking water standard.

Comparing Aquifer Remediation Strategies

Two primary measures were used for comparison of different remediation designs: the total time taken to achieve cleanup and the total volume of contaminant mass extracted from the aquifer. These are hereafter referred to as the cleanup time and the cleanup mass respectively. Initially a pore volume (∇_p) analysis was conducted to assess the normalized volume of water extracted for the rate-limited sorption models with an LEA model. The ultimate measure of cleanup effectiveness would include an economic analysis of remediation costs. During the entire time of remediation, for instance, there

are costs associated with operating and maintaining the ground water extraction, treatment and monitoring systems, in addition to initial capital outlays for the equipment and associated startup costs. Conceptually, lower pumping rates may require different equipment and thus would affect the overall cost of the system. For purpose of this analysis all capital and operating costs were assumed to be the same. Thus, cost optimization was beyond the scope of this thesis and efficiency will be viewed in terms of the strategy which yields the greatest mass of contaminant during the pumping period. This strategy was chosen for the following reasons: total pumping time as a criterion would require attendant economic analysis to distinguish amongst different pumping rates (as higher pumping rates were assumed to remediate the aquifer faster [not necessarily more efficiently] and would always be superior to slower pumping rates); total contaminant removed from the aquifer which was the ultimate criteria which was a consistent factor in all strategies and for either first- or second-order non-equilibrium models.

Non-Equilibrium Effects on Breakthrough Curves

First- and Second-Order Pulsed Pumping Comparison

General

Pulsed-pumping was previously defined as a possible improvement on continuous pumping. Pulsed-pumping is attractive in that it would allow time during the rest cycle for the sorbed solute to desorb into the mobile regions for later extraction. A comparison was made between the mass extraction efficiency and breakthrough arrival times for the two methods of modeling physical, rate-limited sorption. Rest periods for the "off-cycle" of the pumps were held constant and were reflective of the inverse ratio of the diffusion coefficient to the square of the immobile region radius [$1/(a^2/D_e)$]. This criterion is

similar, but of lesser magnitude than that postulated by Goltz and Roberts [1986a:87] as represented by the equation $1/\alpha$. Use of the a^2/D_e ratio provided a simple means of defining rest periods for both first- and second-order methods. This ratio is reflective of the time scale required to diffuse contaminant out of the immobile region. First-order rate constants were calculated using Equation (3.29) and comparative rest periods for the immobile zones are shown in Table 4.2 for both cases.

Pumping periods were variable and the cessation of pumping standard was based on observation of the time at which the mobile region concentration decreased below the cleanup standard previously defined ($0.05\mu\text{g/l}$). These were arrived at in an iterative manner through an observational approach, whereas, rest periods were fixed throughout the simulation.

A total of 1500 simulations were conducted using first- and second-order cases in the range of D_e/a^2 values outlined in Table 4.2 for pumping rates of 100 to $600\text{ m}^3/\text{day}$. Examination of the extreme cases, for both small and large De/a^2 ratios, was accomplished through breakthrough curve analysis and integration of portions of breakthrough curves which corresponded to pumping periods with concentrations above the cleanup standard to find the cleanup mass extracted. Appendix D contains the remainder of the intermediate breakthrough curves which were not examined quantitatively.

Pore Volume Analysis

The total pore volume (∇_p) within the plume was estimated by the equation [Valocchi, 1986:1689]:

$$V_p = \pi r_p^2 b n \quad (4.5)$$

This provided an estimate of the total time required to pump the mobile zone free of contaminated water and replace it with clean water. Using Equation (4.5) the pore volume for the contaminant plume under study was 1620.31 m³. Table 4.3 summarizes the pore volumes required to treat the simulated "sandy" aquifer using an equilibrium model under continuous pumping, and first- and second-order diffusion models under pulsed-pumping conditions.

TABLE 4.2
COMPARATIVE REST PERIODS FOR D_e/a^2 RATIOS AND
FIRST-ORDER RATE CONSTANTS

$\frac{D_e}{(m^2/d)}$	a (m)	$\frac{D_e/a^2}{(d^{-1})}$	α (d ⁻¹)	$T_{rest} \frac{(a^2/D_e)}{(d)}$	$T_{rest} \frac{(1/\alpha)}{(d)}$
1.2×10^{-5}	0.05	0.005	5.8×10^{-8}	208.16	198.67
2.25×10^{-5}	0.05	0.009	1.1×10^{-7}	111.29	106.21
1.2×10^{-5}	0.03	0.013	1.6×10^{-7}	74.94	71.52
3.5×10^{-5}	0.05	0.014	1.7×10^{-7}	71.44	68.18
2.25×10^{-5}	0.03	0.025	3.0×10^{-7}	40.06	38.24
3.5×10^{-5}	0.03	0.039	4.7×10^{-7}	25.72	24.54
1.2×10^{-5}	0.01	0.12	1.5×10^{-6}	8.32	7.95
2.25×10^{-5}	0.01	0.225	2.7×10^{-6}	4.45	4.25
3.5×10^{-5}	0.01	0.35	4.2×10^{-6}	2.86	2.73

TABLE 4.3
COMPARISON OF EXTRACTED PORE VOLUME TO ACHIEVE CLEANUP

<u>D_e/a^2</u> <u>Ratio</u>	<u>Unmod</u> <u>SUTRA</u>			<u>1st-</u> <u>Order</u>			<u>2nd-</u> <u>Order</u>		
	<u>Q=100</u>	<u>Q=400</u>	<u>Q=600</u>	<u>Q=100</u>	<u>Q=400</u>	<u>Q=600</u>	<u>Q=100</u>	<u>Q=400</u>	<u>Q=600</u>
0.005	2.3	2.3	2.4	3.5	7.0	8.6	2.8	2.9	3.0
0.009	2.3	2.3	2.4	2.9	5.0	6.2	2.6	2.9	3.0
0.013	2.3	2.3	2.4	2.8	4.1	5.0	2.6	2.9	3.0
0.014	2.3	2.3	2.4	2.8	4.0	4.9	2.6	2.9	3.0
0.025	2.3	2.3	2.4	2.7	3.2	3.7	2.4	2.8	2.9
0.039	2.3	2.3	2.4	2.7	2.9	3.1	2.4	2.7	2.9
0.12	2.3	2.3	2.4	2.7	2.6	2.7	2.4	2.4	2.5
0.225	2.3	2.3	2.4	2.7	2.6	2.7	2.4	2.3	2.4
0.35	2.3	2.3	2.4	2.7	2.6	2.6	2.3	2.3	2.4

We can make the following observations from the data in Table 4.3:

a. Both first- and second-order diffusion models required pumping of pore volumes which approached that of the equilibrium model (SUTRA unmodified) at higher D_e/a^2 ratios.

b. The second-order diffusion model was more precise in matching the extraction volume attained by the equilibrium model at the highest D_e/a^2 value.

c. The first-order diffusion model required treatment of more pore-volumes of ground water to achieve the same cleanup level as the second-order model.

d. The equilibrium model could model breakthrough behavior for all pumping rates examined at the higher D_e/a^2 values.

Spherical Diffusion

The second-order diffusion model was governed by the flux produced by the immobile zone. Figure 4.3 illustrates the gradients at various points in time for the immobile zone. The left side of the graph represents the center of the immobile zone, while the right side of the graph represents the exterior of the sphere, which is in equilibrium with the mobile zone concentration. The upper portion of the graph represents the highest concentrations within the immobile region, while the lower regions of the graph represent an area where the model will seek equilibrium with the mobile zones.

At the start of pumping the immobile zone concentration was at equilibrium with the mobile fluid concentration. This constant concentration throughout the zone is depicted with the linear concentration profile at the initial time step ($T = 0$ days) on Figure 4.3. Upon completion of the first pumping cycle ($T = 41.6$ days), the immobile zone had discharged contaminant slowly and the outer elements of the immobile zone mesh had decreased in concentration, while the interior elements remained at higher levels.

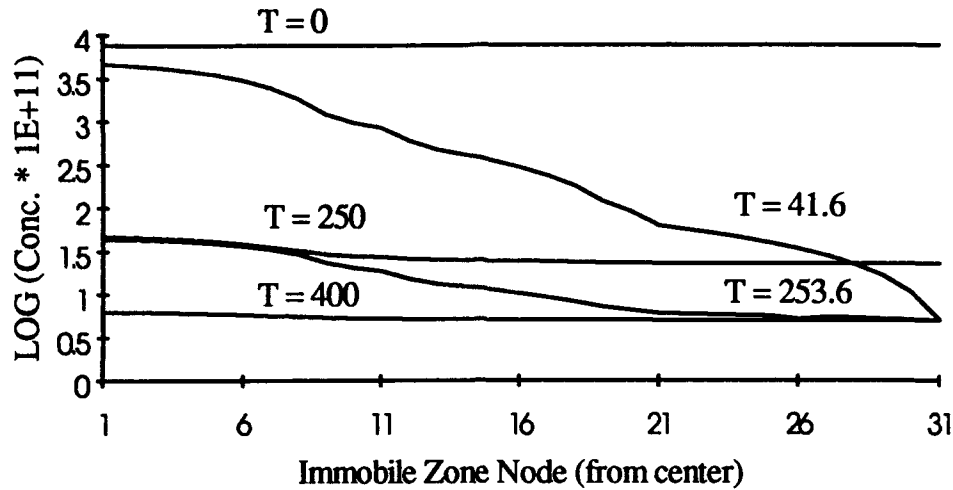


Figure 4.3. Low Pumping Rate Immobile Region Concentration Profiles
 $(Q = 100 \text{ m}^3/\text{day})$ $(D_e/a^2 = 0.005)$ (Time [T] is in units of days)

The boundary condition (Equation [3.27]) that required the concentration at element 31 (outer node of immobile zone) to be in equilibrium with the mobile zone was confirmed by the asymptotically decreasing concentration gradient which terminated at the concentration of the mobile zone. The pump was then turned off and the concentration profile at the end of a rest cycle ($T = 250$ -days) was approaching an intermediate, equilibrium point, as depicted in Figure 4.3 by the small slope in this profile. This transient occurred because all elements within the immobile zone were diffusing or absorbing concentration fluxes (as contaminant mass moved from an area of higher concentration to one of lower concentration) in an effort to equilibrate at the same concentration. The net result of this equilibrium seeking behavior was a decreasing flux out of the immobile zone, as the concentration gradient decreased due to a rise in the mobile zone concentration with subsequent changes in the outer nodes of the immobile zone mesh.

The pump was then turned on again (due to the rebound in concentration observed within the mobile zone [as shown in Figure 4.4]). However, as the concentration of the rebound on completion of the first rest cycle was smaller than the initial concentration of the plume (at start of remediation), it took a shorter time to reduce the concentration of the mobile zone below the action level. This reduction is illustrated by Figure 4.4 below, where at completion of the second pump period ($T = 253.6$ -days) the BTC once again is at the cleanup level.

Finally, after turning the pump off, once again, and allowing the spheres to diffuse slowly out to the mobile zone for another rest period ($T = 400$ -days), the immobile zones had virtually reached equilibrium once again. This rest period was less than the standard period in an effort to limit the focus of study to a cleanup time of less than 400-days for second-order solutions studied. The flux out of the immobile region was very minor and did not cause significant rebound within the mobile region. At this point the aquifer was considered cleaned up, as the mobile region concentration was below the cleanup standard and the immobile region concentration had diffused sufficiently enough that it would contribute a negligible amount of contaminant ($T = 400$ -days in Figure 4.3) to the mobile region for rebound.

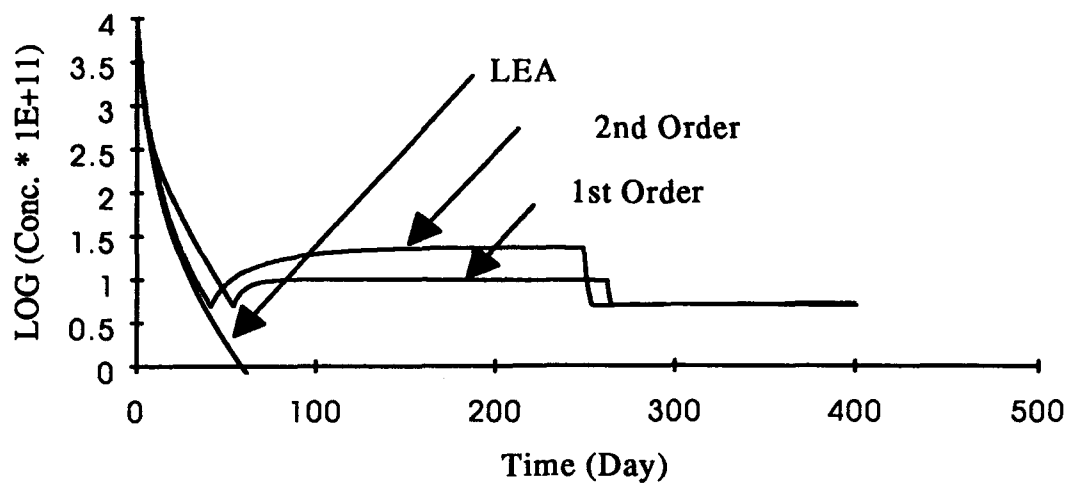


Figure 4.4. First- and Second-Order, Pulsed Pumping Comparison to LEA Model
 $(Q = 100 \text{ m}^3/\text{day}) (D_e/a^2 = 0.005)$

A logarithmic scale is used to enable depiction of complete BTCs. A linear scale would provide only a limited view of the BTC. This relationship is illustrated by Figure 4.5:

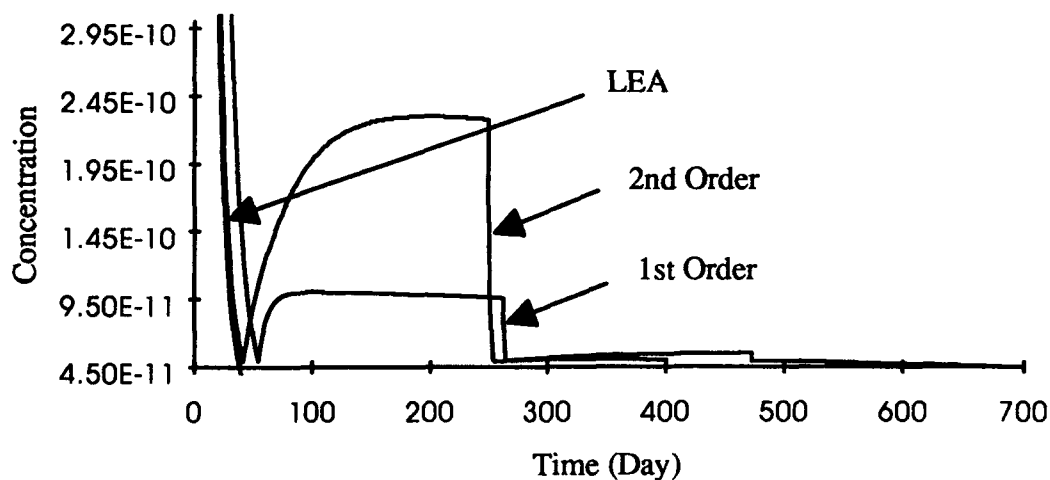


Figure 4.5. First- and Second-Order, Pulsed Pumping Comparison to LEA Model
 $(Q = 100 \text{ m}^3/\text{day}) (D_e/a^2 = 0.005)$

Small D_e/a^2 Ratio Comparison At A Higher Pumping Rate

In the previous analysis (Figures 4.4 and 4.5) a small D_e/a^2 ratio (0.005) was analyzed for a low pumping rate. The immobile zone layered half-width was large (0.05 m) and the effective diffusive rate coefficient (D_e) [$1.2 \times 10^{-5} \text{ m}^2/\text{day}$] was small. Now, a larger pumping rate ($400 \text{ m}^3/\text{day}$) is analyzed. Figure 4.6 illustrates these points:

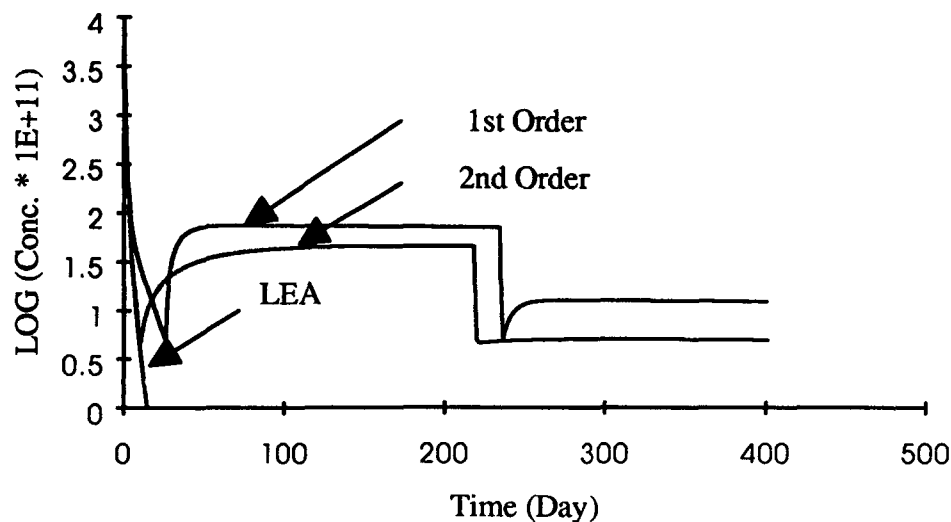


Figure 4.6. First- and Second-Order, Pulsed Pumping Comparison to LEA Model
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)

Analysis of Figure 4.6 indicated the following:

- a. The first- and second-order models were retarded with respect to the LEA model (represented by SUTRA unmodified).
- b. Both first- and second-order models displayed rebound effects after the pumps were turned off. This rebound effect was due to diffusion of contaminant from the immobile zone into the mobile fluid by means of concentration gradient fluxes.

c. The first-order model had a higher rebound level than the second-order model at this pumping rate. As can be seen in Figure 4.4, the reverse was true at the lower pumping rate. At a higher pumping rate the "shutoff concentration" in the mobile zone is reached faster than with the lower pumping rate. Therefore, there has not been as much time for diffusion from the immobile zone during the pumping cycle and thus more mass is remaining within the immobile zone in both models for the higher pumping rate. Accordingly, higher rebound thresholds are achieved for both models at the higher pumping rate. Apparently, at the $Q = 100 \text{ m}^3/\text{day}$ pumping rate, during the first pumping cycle ($T = 41.6$ days in Figure 4.4), more mass moved out of the first order immobile zones than the second-order models prediction for the same case. With the $Q = 400 \text{ m}^3/\text{day}$ pumping rate, during the first pumping cycle ($T = 22$ days in Figure 4.6 for the first-order case) the reverse is true.

d. The first-order case appeared to reach equilibrium faster than the second-order case, as illustrated by the sharp flattening in its concentration profile. The second-order model slowly reached its equilibrium point. This result is intuitive as the immobile zone nodes seek equilibrium within themselves and with the concentration of the mobile water surrounding them, acting as sinks and reservoirs for concentration amongst the immobile zone and slow the rise in concentration within the mobile zone.

e. Departure from equilibrium in both cases was rapid and evident by the time one pore volume of ground water (4.05-days) had been extracted. This result was also observed by Brogan [1991:39].

In Figure 4.6 the LEA case (SUTRA unmodified) appeared to achieve the same concentrations, at the same time, as the second-order case. However this apparent convergence was due to the graphical resolution. Figure 4.7 illustrates this point.

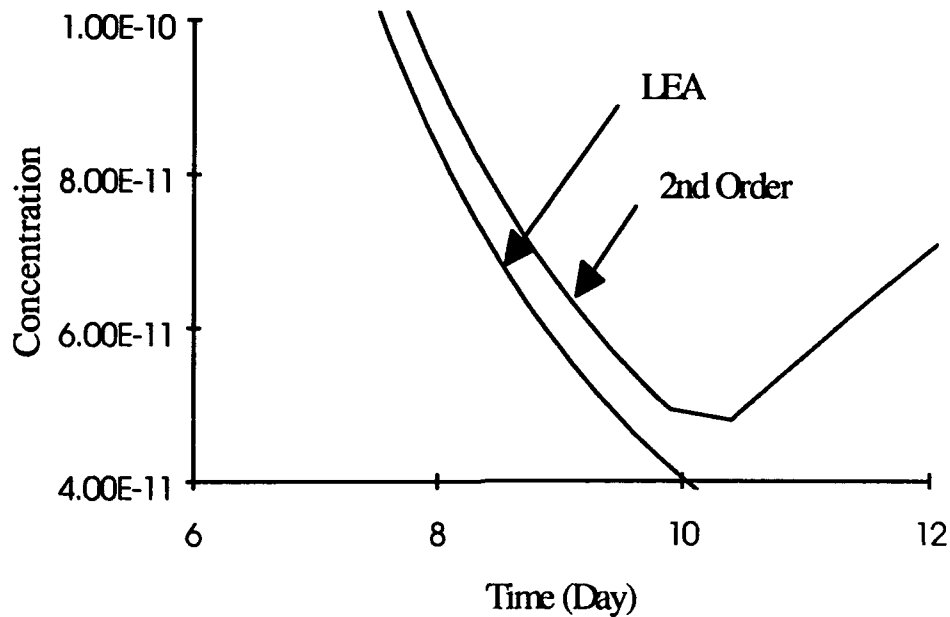


Figure 4.7. SUTRA Unmodified Comparison to Second-Order Diffusion Model
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$)

The effect of an even higher pumping rate ($600 \text{ m}^3/\text{day}$) was to reduce the cleanup time it would take to achieve breakthrough, yet greater pore volumes would be extracted to achieve cleanup to the same standard within the aquifer. Figure 4.8 illustrates the breakthrough curves for first and second order pulsed-pumping.

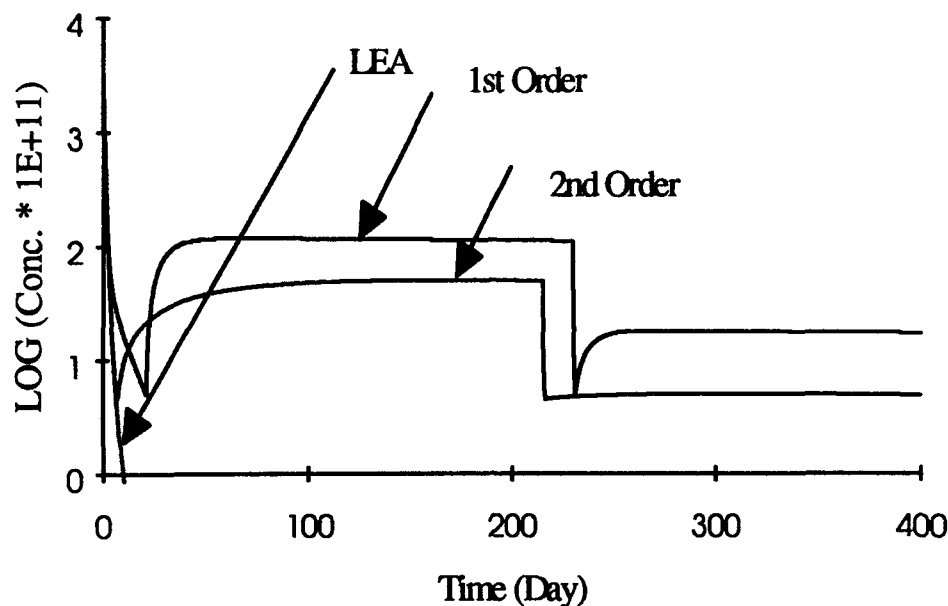


Figure 4.8. First- and Second-Order, Pulsed Pumping Comparison to LEA Model
 $(Q = 600 \text{ m}^3/\text{day}) (D_e/a^2 = 0.005)$

Analysis of Figure 4.8 was as follows:

a. The first-order models breakthrough was delayed with respect to the second-order model (as in the $Q = 400 \text{ m}^3/\text{day}$ case) due to the relatively constant ΔC flux inherent in the first-order models algorithm.

b. The second-order model achieved breakthrough earlier due to the limited diffusion which occurred from the immobile regions during the time the pumping was occurring. This result is expected since the advective time scale is much shorter than the diffusion time scale for this case. Furthermore, physically the behavior is realistic because higher pumping rates flush the mobile zone clear of contaminant with clean water quickly

(faster mobile zone velocity) before the spherical pore elements discharged into the mobile zone (slow diffusive velocity). The net effect within the immobile regions elements was to induce a sharper concentration gradient in concentration within the outer elements of the immobile region mesh as nodes discharged a flux to maintain the boundary conditions (Equations [3.27] and [3.28]).

c. The first-order model discharged more contaminant from the immobile zones in retarding the breakthrough curve during pumping, yet predicted a larger rebound after the pumping was terminated. This illustrated the counter-intuitive nature of the first-order model in this case.

d. First-order diffusion displayed a consistently higher rebound than second-order diffusion at the higher pumping rate. This larger rebound would result in more pore volumes removed (by the first-order model) to achieve the cleanup standard than the same second-order case (as confirmed by Table 4.3).

e. First-order models reached equilibrium quicker than second-order diffusion models did.

f. After one pore volume (2.7-days) had been removed, first-order models appeared to diverge from the second-order solution.

g. The second pulsed-pump period for the second-order model was less than the corresponding first-order model pumping period.

The effect of the larger pumping rate within the immobile region was to induce a sharper gradient in the concentration profile for the outer elements of the immobile region mesh as nodes discharged a flux to maintain the equilibrium boundary condition. This gradient was illustrated in Figure 4.9 by the $T = 6.7$ day profile. This represented the immobile zone concentration upon completion of pumping. In that case, the inner immobile region elements had previously maintained concentration at higher levels and the lower, intermediate equilibrium point reached was higher than that in the $100 \text{ m}^3/\text{day}$ pumping case illustrated by Figure 4.3. When the pump was turned on again a greater pore volume extraction (0.48) was required to reach the cleanup standard than that of the lower pumping-rate case (0.24). The net effect as illustrated in Table 4.3 was that higher pumping rates must extract higher pore volumes of water to achieve the same cleanup level at low D_e/a^2 values as lower pumping rates.

Appendices E and F tabulate the pumping strategies required to achieve cleanup by both the first- and second-order methods for all pumping rates and D_e/a^2 ratios examined. These simulations confirmed that after a second pulsed pump period, the second-order model did not display any significant rebound effects for the low and high-pumping rates previously examined, whereas the first-order model continued to require successive pumping and rest periods to achieve the cleanup standard. This resulted in markedly different cleanup times for the two non-equilibrium models examined. Table 4.4 illustrates the difference in cleanup time for the pumping rates used in this case.

TABLE 4.4
CLEANUP TIME FOR LOW D_e/a^2 RATIO (0.005)

<u>Pumping Rate</u> (m ³ /day)	<u>Cleanup Time</u>	<u>Cleanup Time</u>
	<u>First-Order Model</u> (days)	<u>Second-Order Model</u> (days)
100	473	254
400	643	220
600	648	216

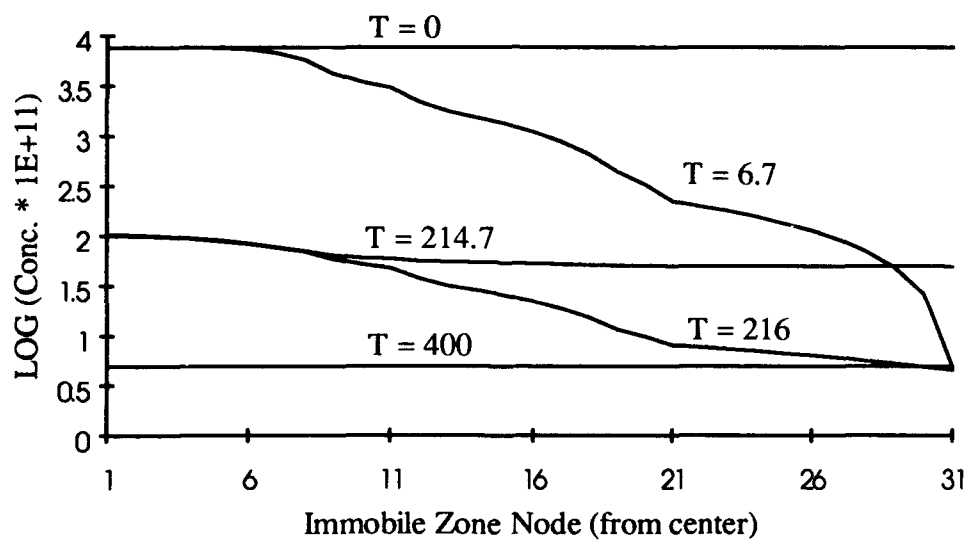


Figure 4.9. High Pumping Rate Immobile Region Concentration Profiles
($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.005$) (Time [T] is in units of days)

Large D_e/a^2 Ratio Case Comparison

In the case of a large D_e/a^2 ratio (0.35) small layered half-widths (0.01 m) were assumed to have a large effective diffusion coefficient (D_e) ($3.5 \times 10^{-5} \text{ m}^2/\text{day}$).

Figures 4.10, 4.12 and 4.13 illustrate the breakthrough curves for the three pumping rates examined. The following observations were made by analysis of the breakthrough curves and Appendices E and F for the high D_e/a^2 ratio:

a. The breakthrough curves for all the cases exhibited little difference between the first- and second-order models and both non-equilibrium models compared closely with the LEA model until the initial breakthrough concentration was achieved. Thereafter, the non-equilibrium models exhibited tailing, while the LEA model continued to predict decreased concentrations. These similarities occurred when case Peclet numbers for the various pumping rates were the largest of those studied and were approaching the limit of the non-equilibrium region where molecular effects have influence on dispersion within the mobile zone. This result illustrated that Peclet number may not be as valid a measurement of non-equilibrium effects as D_e/a^2 .

b. The first-order model predicted minor rebound in this case, which was not predicted by the second-order model (as found in Appendices E and F). The negligible rebound, due to rapid dissipation of the immobile zone solute, was confirmed when the immobile region concentration profile was examined. In this case, the large diffusion coefficient barely retarded movement of the contaminant out of the immobile region into the mobile zone. Thus pumping of the mobile zone served to remove contaminant equally as well from the immobile region due to the smaller diffusive time scale (2.86-days from Table 4.2). At the end of the first pumping period ($T = 37.7$ days in Figure 4.11 and $T = 6.5$ day in Figure 4.14) the contaminant in the immobile region had virtually all moved into the mobile zone and there was almost no flux of contaminant out of the immobile region to facilitate rebound, due to depletion of mass in the immobile region during pumping.

c. LEA modeling could adequately model breakthrough and first- or second-order models do not lend greater accuracy in results for the computational effort required.

d. Pulsed pumping in this case would not promote greater efficiency. Continuous pumping (at all pumping rates) for this D_e/a^2 ratio, removed approximately the same number of pore volumes (from Table 4.3) of ground water to achieve cleanup of the aquifer as pulsed-pumping. Use of another optimization factor (other than pore volumes removed) such as total pumping time or economic factors would be more appropriate in this case. Table 4.5 tabulates the cleanup time required by continuous pumping to remediate the aquifer under these conditions.

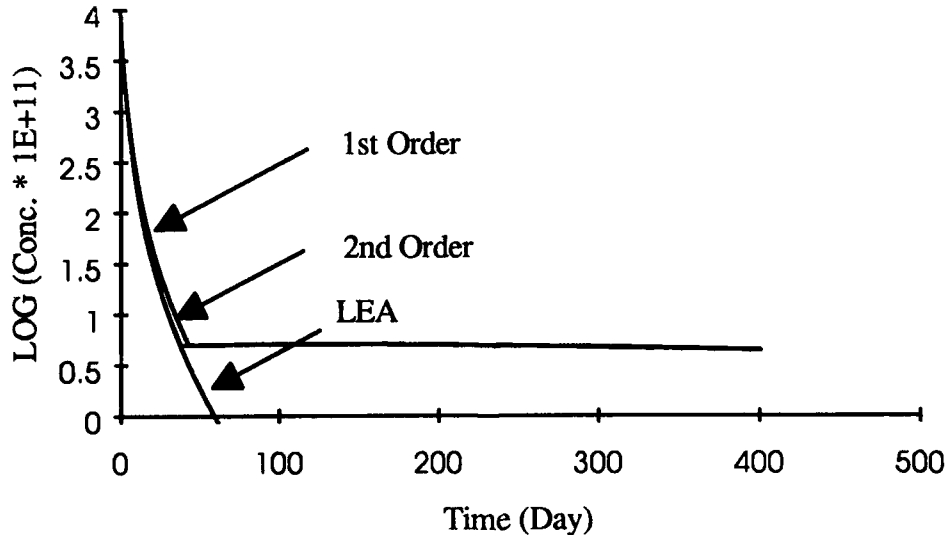


Figure 4.10. First- and Second-Order, Pulsed Pumping Comparison to LEA Model
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$)

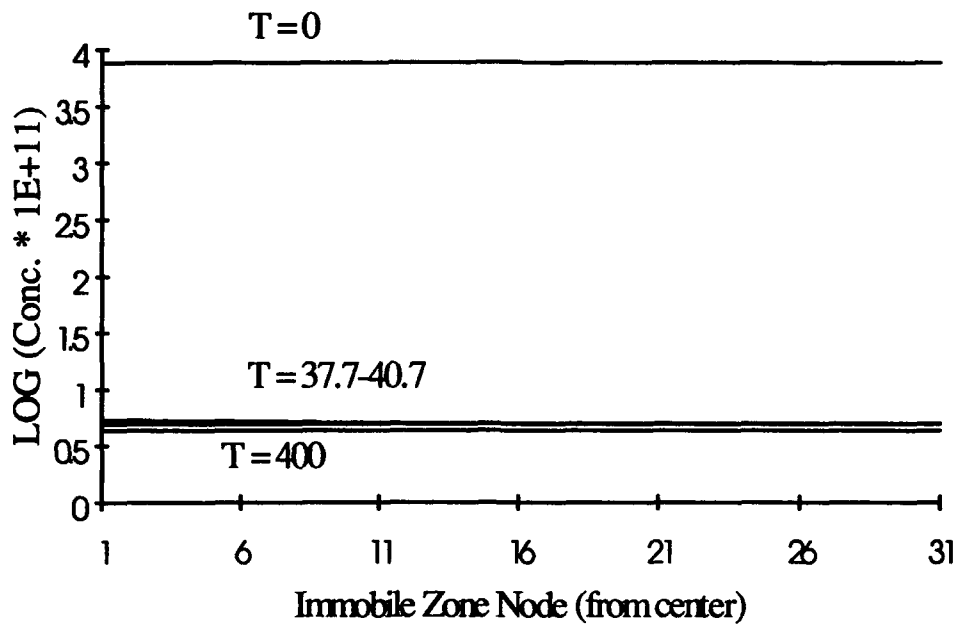


Figure 4.11. Low Pumping Rate Immobile Region Concentration Profiles
 $(Q = 100 \text{ m}^3/\text{day})$ $(D_e/a^2 = 0.35)$ (Time [T] is in units of days)

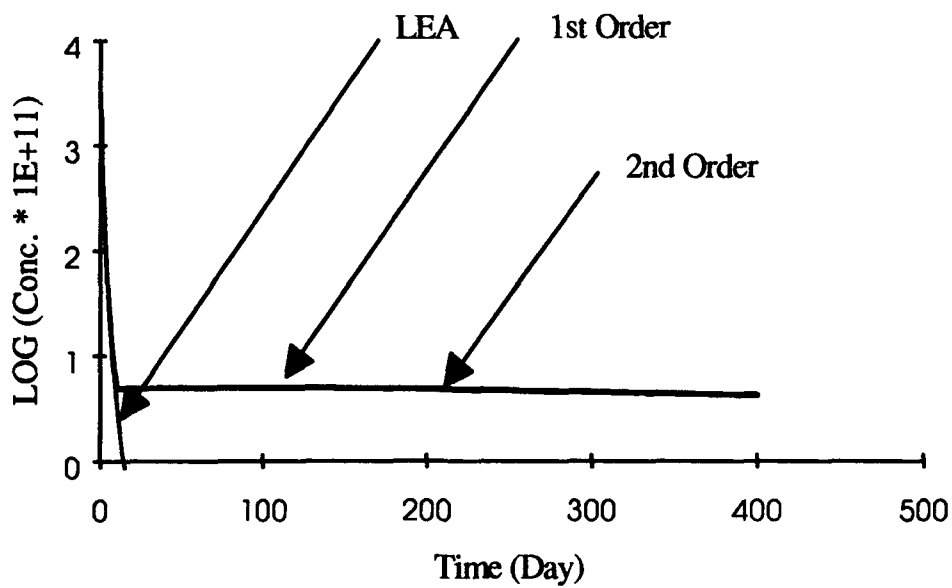


Figure 4.12. First- and Second-Order, Pulsed Pumping Comparison to LEA Model
 $(Q = 400 \text{ m}^3/\text{day})$ $(D_e/a^2 = 0.35)$

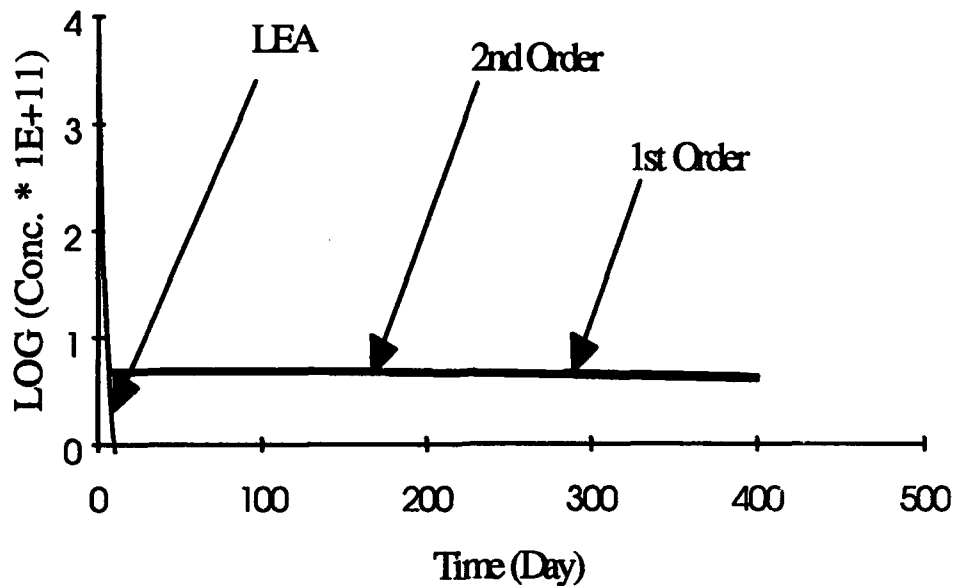


Figure 4.13. First- and Second-Order, Pulsed Pumping Comparison to LEA Model ($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$)

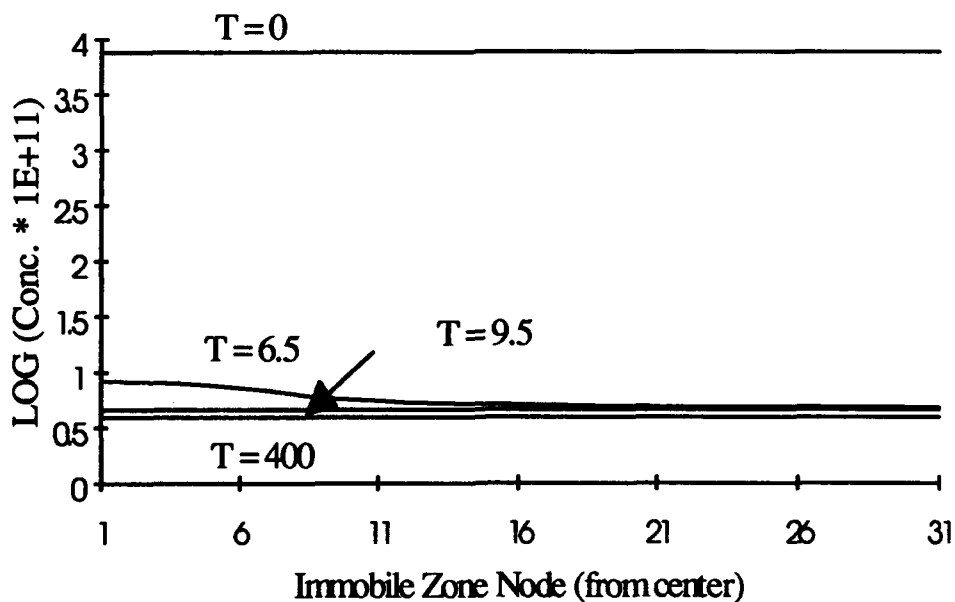


Figure 4.14. High Pumping Rate Immobile Region Concentration Profiles ($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.35$) (Time [T] is units of days)

TABLE 4.5
CLEANUP TIME FOR HIGH D_e/a^2 RATIO (0.005)

<u>Pumping Rate</u> (m ³ /day)	<u>Cleanup Time</u> <u>First-Order Model</u> (days)	<u>Cleanup Time</u> <u>Second-Order Model</u> (days)
100	46.1	37.7
400	13.5	9.5
600	10.0	6.5

Summary

Up to this point we have been solely concerned with cleanup time and breakthrough curve analysis. A summary of what has been discussed so far is:

- a. For high D_e/a^2 ratios, LEA models may provide an efficient means of estimating cleanup time, while non-equilibrium models may more effectively predict tailing than the LEA model.
- b. If the objective was rapid cleanup and an LEA model applied, then higher pumping rates with continuous pumping may prove to be the most effective strategy.
- c. Pulsed-pumping at lower pumping rates resulted in a longer cleanup time for the aquifer, but required a reduced pore volume to be extracted from the aquifer, when low D_e/a^2 ratios applied.

d. First-order models may over- and under-predict rebound within the aquifer, require treatment of more pore volumes and predict longer cleanup times than second-order models for low D_e/a^2 ratios.

Pumping Strategy Comparison

We now examine various strategies for a single pumping situation using the second-order model in an effort to determine optimality for cleanup mass and cleanup time. This analysis examined a continuous pumping case, a pulsed-pumping case, and a continuous, effective pumping rate case for a single D_e/a^2 ratio (0.005).

A continuous, effective pumping rate (Q_{eff}) can be hypothesized once the pulsed-pumping rates are determined or arrived at iteratively. Brogan [1991:137] defined the effective pumping rate as the cleanup volume divided by the cleanup time:

$$Q_{eff} = \frac{Q_w * \sum T_{pump}}{\sum T_{pump} + \sum T_{rest}} \quad (4.6)$$

The continuous, effective pumping rate must provide for containment of the contaminant plume to be considered truly effective. Another factor in its formulation was that the pulsed-pumping rate must have been determined already to facilitate this calculation. Finally, the continuous, effective pumping rate ensures that the same cleanup volume is extracted from the aquifer as pulsed-pumping methods. However, it may extract less cleanup mass than the pulsed method (higher rate). Fickian Diffusion will be used in the following calculations as was discussed in Chapter II and shown in this Chapter. First-order methods may over predict mass in the immobile zones at high pumping rates and

may not accurately simulate diffusion in high flow situations or in cases with small sampling scale relative to the diffusion rate. Finally, second-order (Fickian) diffusion methods are more firmly founded on a physical basis. Figure 4.15 illustrates the pumping strategies that will be compared for cleanup efficiency:

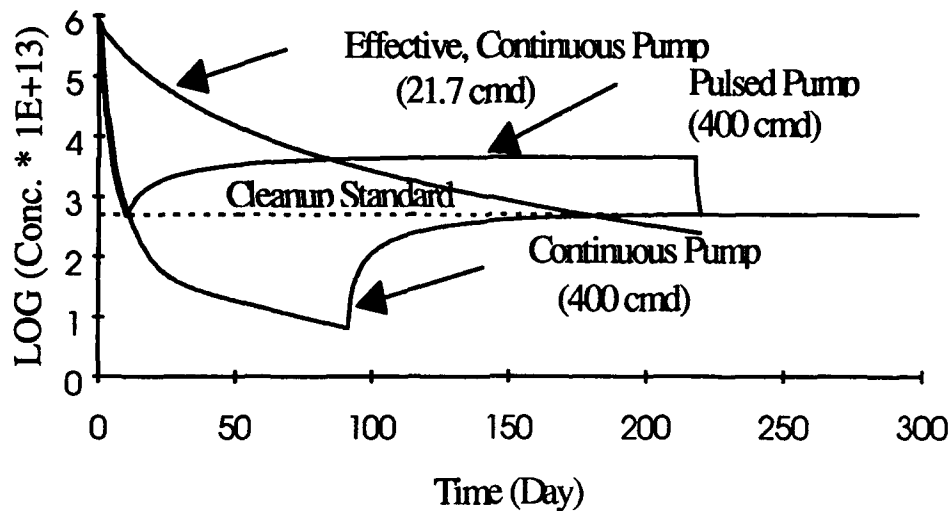


Figure 4.15. Pumping Strategy Comparison ($D_e/a^2 = 0.005$)

Cleanup mass was determined by composite trapezoid integration [Burden and Faires, 1993:187] of areas under the concentration curves which were above the cleanup standard for the various strategies. It is uneconomical to treat water which was pumped from areas with concentrations below the cleanup standard and these areas were not considered to contribute to the overall cleanup mass extracted from the aquifer. An additional problem with this method, which isn't explored is what becomes of the treated water (or untreated in case of continuous pumping at levels below the cleanup standard), as some authorities may not allow re-injection of the pumped water into the aquifer again.

The total cleanup mass is arrived at by use of the following equation:

$$M_{\text{cleanup}} = \sum_1^n \rho Q_w \frac{h}{2} [C(a) + C(b) + 2 \sum_{j=1}^{m-1} f(x_j)] \quad (4.7)$$

where $h = (b-a)/m$; m is the number of subintervals between the pumping times represented by b = time ended and a = time started; $x_j = a + jh$ for each $j = 0, 1, \dots, m$; and n is the pumping period number. Based on the injection rate of $5.0 \text{ m}^3/\text{day}$ at a concentration of $5.0 \text{ } \mu\text{g/l}$ for 100 days it was estimated that $5.0 \times 10^{-2} \text{ kg}$ (assuming all is converted to dissolved or sorbed solute) of contaminant entered the ground water.

Table 4.6 outlines the mass extracted per day by the respective pumping strategies. While the continuous pumping strategy achieves breakthrough at the same time as the second-order pulsed-pumping case, it must continue to extract water with contaminant diluted within this standard (at lower concentrations) to effectively clean the aquifer up. The continuous pumping strategy required extraction of a larger number of pore-volumes (22.3) to achieve the same level of cleanup as that achieved by the pulsed-pumping strategy (2.9). This is the result of the slow diffusion of contaminant out from the immobile zone into the mobile fluid. In essence the continuous pumping case is diluting clean water with low levels of contaminant which have slowly diffused from the immobile zone as a mass flux.

TABLE 4.6
MASS EXTRACTION PUMPING STRATEGIES
($D_e/a^2 = 0.005$)

<u>Pumping Strategy</u>	<u>Mass per Day Extracted (kg/Day)</u>	<u>Pore Volumes Extracted</u>	<u>Total Cleanup Time (Days)</u>	<u>Total Pumping Time (Days)</u>
Pulsed-Pumping	1.3×10^{-3}	2.9	219.5	11.7
Continuous Pump	2.3×10^{-4}	22.3	90.3	90.3
Continuous, Effective Pumping	6.6×10^{-5}	2.9	219.5	219.5

The following conclusions may be made from Tables 4.3 and 4.6; and Figure 4.15:

- a. Pulsed-pumping and continuous, effective pumping had the same cleanup time, but different cleanup mass extracted.
- b. Continuous pumping had a significantly longer pumping time than pulsed-pumping as opposed to cleanup time, where the reverse is true.
- c. Terminating the continuous pumping case when the cleanup standard was achieved would result in the rebound exhibited by the pulsed case within the matrix, thus prolonging cleanup time beyond that predicted by the continuous case.

d. Continuous pumping required remediation of more pore volumes (22.3) of ground water than either continuous, effective pumping or pulsed-pumping (2.9). This would have a major effect on an economic analysis because of the large volume of ground water extracted by the continuous method which would require special handling and disposal, if current practice by regulatory authorities continues to prohibit re-injection of pumped water, whether treated or not..

e. Continuous, effective pumping extracted less cleanup mass than either pulsed-pumping or continuous pumping strategies.

f. Pulsed-pumping was the most efficient method in extracting mass per unit volume pumped or per day, while continuous pumping extracted more mass (although the majority of the difference between this method and pulsed pumping was in water extracted at concentrations below the cleanup standard).

g. Continuous pumping required the shortest cleanup time of the three strategies studied, but required 7.7 times more pumping time than pulsed pumping.

V. Conclusions and Recommendations

This concluding chapter draws together the research presented in the previous chapters. It begins with an overview of the research effort. Next, it summarizes the findings of this study, and finally, it lists recommendations for model improvements and for follow-on research.

Overview

The focus of this research was to model the fate and transport of contaminated ground water under conditions of rate-limited sorption. The modification of the SUTRA code was based on rugged and well tested code, which IRP managers can use to better estimate the cleanup time, mass extracted, plume retardation, and rebound or tailing effects when considering a pump-and-treat extraction system for remediation. The main thrust of the model's evaluation was to study its performance under a range of realistic parameters and to examine the differences in cleanup criteria for LEA, first- and second-order diffusion models. In the latter case, demonstration of the variability in predicted results among the various models was a critical objective. This objective was accomplished through numerous simulations of a pulsed-pumping extraction system using the LEA and first-order models and contrasting their performance with respect to the physically and computationally more accurate second-order model.

The literature review clearly revealed that research during the past two decades had contributed to a greater understanding of rate-limited sorption at the laboratory and in limited field scale experiments. This progress had greatly enhanced the study and

modeling of transport processes and impacts on treatment technologies for contaminated aquifers. A large number of models had been postulated and marketed over the years. Models that emulated rate-limited diffusion equations were found to be primarily analytical in nature and highly specialized for the system studied. Two other authors had modeled chemical non-equilibrium processes. However, no software packages have been marketed to aid IRP managers and field workers in modeling remediation projects which incorporate this behavior. Pulsed-pumping had been the subject of speculative literature, concerning its applicability, with some authors asserting its non-effectiveness over conventional methods of pump-and-treat systems.

This research formulated a modification to the SUTRA code for physical, non-equilibrium rate-limited sorption. The code was modified to incorporate both first-order and second-order rate-limited sorption methods. The modified code was validated for both sorption models with an analytical code and through incorporating previously tested modules and routines. An extensive series of simulations was conducted to evaluate performance of a pulsed-pumping extraction system in remediation of a hypothetical aquifer, using realistic parameters. Simulations modeled sorption by assuming either equilibrium or rate-limited conditions existed with the rate-limitation described by either a first-order equation or by Fickian diffusion of contaminant through a spherical immobile region. Additionally, these simulations evaluated cleanup performance for three traditional approaches to pump-and-treat remediation and assessed the applicability of this code and remediation strategies.

Summary of Findings

Simulations were used to demonstrate the capability and viability of the model modification. In addition, a comparison of this model's simulations to those of another model, which had recently been validated against other codes, was conducted with favorable results. Model simulations that were conducted revealed the following:

a. A pulsed-pump operation may allow for more efficient removal of contaminant mass per unit volume, while pumping for less time than conventional continuous pumping methods. The model clearly demonstrated the rebound and tailing behavior for either first- or second-order (Fickian) diffusion models which are characteristic of the slow desorption processes.

b. The pulsed-pump simulations showed lower pumping rates required less pore volumes of ground water required removal from the aquifer when compared to higher pulsed, pumping rate cases.

c. First-order model predictions of rebound concentrations and cleanup time for aquifers differ significantly from that predicted by second-order methods for low D_e/a^2 ratios for all pumping rates evaluated.

d. First-order models reached equilibrium faster than the second-order models and consequently required shorter rest-cycles than the second-order model to diffuse contaminant into the mobile region.

e. At small D_e/a^2 ratios, higher pumping rates cleaned up the aquifer faster than low pumping rates.

f. LEA methods could model breakthrough behavior at high D_e/a^2 ratios for all pumping rates simulated, since no significant rebound occurred, although first-order methods would be adequate for modeling the tailing behavior.

g. Continuous, effective pumping did not extract as much contaminant mass as either continuous pumping or pulsed pumping methods and required more total pumping time than either method to achieve the cleanup level.

h. Continuous pumping at a high rate extracted more contaminant mass and achieved cleanup quicker than either pulsed or continuous, effective pumping methods, in terms of total remediation time.

Recommendations

As discussed in chapters III and IV, the code was not optimized for computational speed, which ultimately impacted on the size of aquifer and contaminant concentrations modeled. Therefore, the primary emphasis for future research should be to increase the computational speed of the code and to evaluate its performance at field scale on an actual remediation site. More specifically, emphasis should be focused in the following areas:

a. Evaluate performance of the modified code in emulating higher concentration, contaminant movement and retardation during a field tracer test. This would provide a

much needed assessment on the viability of the model and its accuracy for use in modeling other IRP sites.

- b. Extend the code to model multi-species transport in a 2-D aquifer.
- c. Conduct a thorough evaluation of pulsed-pumping strategies versus continuous pumping methods in optimization of pump placement and optimal pumping rates or rest periods for maximum efficiency.
- d. Evaluate model performance in simulating contaminant transport in a heterogeneous aquifer with spatially variable immobile zone radii, diffusion coefficients, porosities and hydraulic conductivities.
- e. Incorporate multi-process non-equilibrium (MFNE) routines with second-order diffusion equations within SUTRA to comprehensively model behavior of solutes which exhibit both physical and chemical non-equilibrium.
- f. Evaluate performance of the model in predicting transport of a sorbing solute within fractured media for a nuclear or chemical waste site.

Appendix A: Radial Pumping Test Input Parameters

<u>Input Parameter</u>	<u>Value</u>
$Q_w = QW$	1000 m ³ /d
$b = B$	10 m
$\alpha_L = a_l$	1.2 m
$\theta = THETA$	0.33
$\theta_m = THETAM$	0.2838
$\theta_{im} = THETAIM$.0462
$\rho_s = RHO$	1810 kg/m ³
$\alpha = ALPHA$	$5.8212 \times 10^{-8} \text{ s}^{-1}$
$a = A$.05 m
$D_o = DO$	$8.5 \times 10^{-10} \text{ s}^{-1}$
$D_e = DE$	$1.17 \times 10^{-5} \text{ m}^2/\text{d}$
$C_o = F1$	1.0
$C_{im} = CA$	1.0
CP	-1.0×10^{100}
$f' = EF$	0.4
$K_d = KD$	0
$\phi = PHI$	0.86
$r_p = XF1$	28 m
Δt	0.1 day
Q	46
ρ_w	1000 kg/m ³
β	$4.4 \times 10^{-10} \text{ ms}^2/\text{kg}$
μ	$1.0 \times 10^{-3} \text{ kg/m}^2 \text{ s}^2$

Appendix B: Representative Sandy Aquifer Input Parameters

<u>Parameter</u>	<u>Value</u>
Q_w	100-600 m ³ /d
r_w	0.02 m
b	20 m
ρ_s	1810 kg/m ³
ρ_w	1000 kg/m ³
α_L	1.2 m
α_T	0.1 m
θ	0.33
θ_m	0.2838
θ_{im}	0.0462
D_m	3.75×10^{-5} m ² /d
D_{im}	5.39×10^{-5} m ² /d
k	9.5×10^{-12} m ²
K	6×10^{-5} m/s
dh/dl	0.005
v_o	0.079 m/d
β	4.8×10^{-10} m ² /N
μ	1.0×10^{-3} kg/m ² s ²
ϕ	0.86
V_p	1620.31 m ³
D_e	$1.2 - 3.5 \times 10^{-5}$ m ² /d
a	0.01 - 0.05 m
Δx	1 m
Δt	0.01 - 1.0 d
r_p	8.85 m

Appendix C: Immobile Region Finite Element Mesh

Node	<u>a = 0.05 m</u>	<u>a = 0.03 m</u>	<u>a = 0.01 m</u>
1	0.000	0.000	0.000
2	0.005	0.003	0.0010
3	0.010	0.006	0.002
4	0.015	0.009	0.003
5	0.020	0.012	0.004
6	0.025	0.015	0.005
7	0.030	0.018	0.006
8	0.035	0.021	0.007
9	0.040	0.024	0.008
10	0.042	0.0252	0.0084
11	0.043	0.0258	0.0086
12	0.045	0.027	0.0090
13	0.046	0.0276	0.0092
14	0.0465	0.0279	0.0093
15	0.0470	0.0282	0.0094
16	0.0475	0.0285	0.0095
17	0.0480	0.0288	0.0096
18	0.0485	0.0291	0.0097
19	0.0490	0.0294	0.0098
20	0.04925	0.02955	0.00985
21	0.04950	0.02970	0.00990
22	0.04955	0.02973	0.00991
23	0.04960	0.02976	0.00992
24	0.04965	0.02979	0.00993
25	0.04970	0.02982	0.00994
26	0.04975	0.02985	0.00995
27	0.04980	0.02988	0.00996
28	0.04985	0.02991	0.00997
29	0.04990	0.02994	0.00998
30	0.04995	0.02997	0.00999
31	0.05	0.03	0.01

Appendix D: Breakthrough Curves

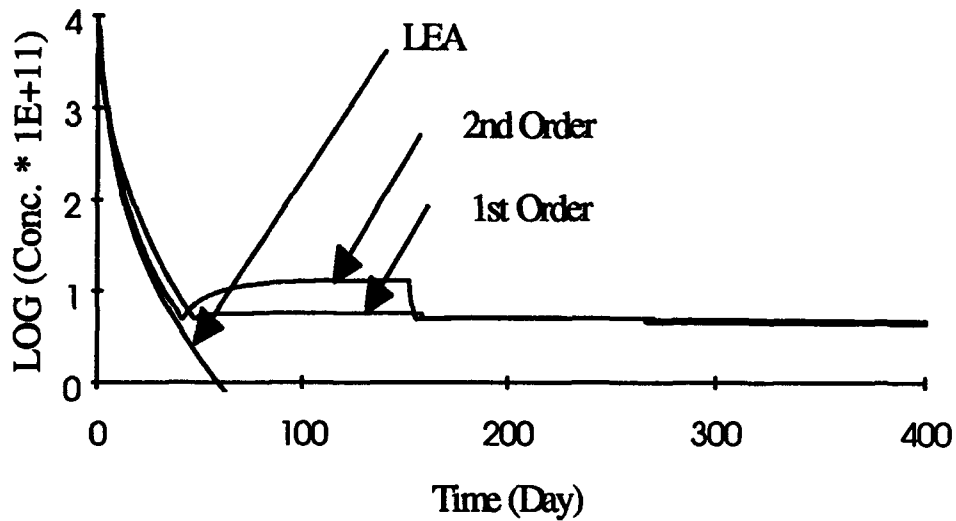


Figure D.1. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.009$)

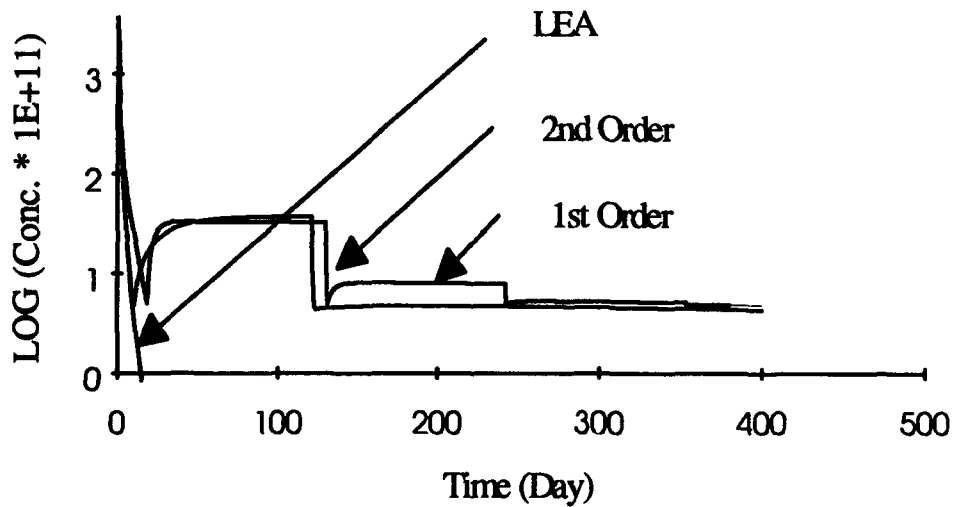


Figure D.2. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.009$)

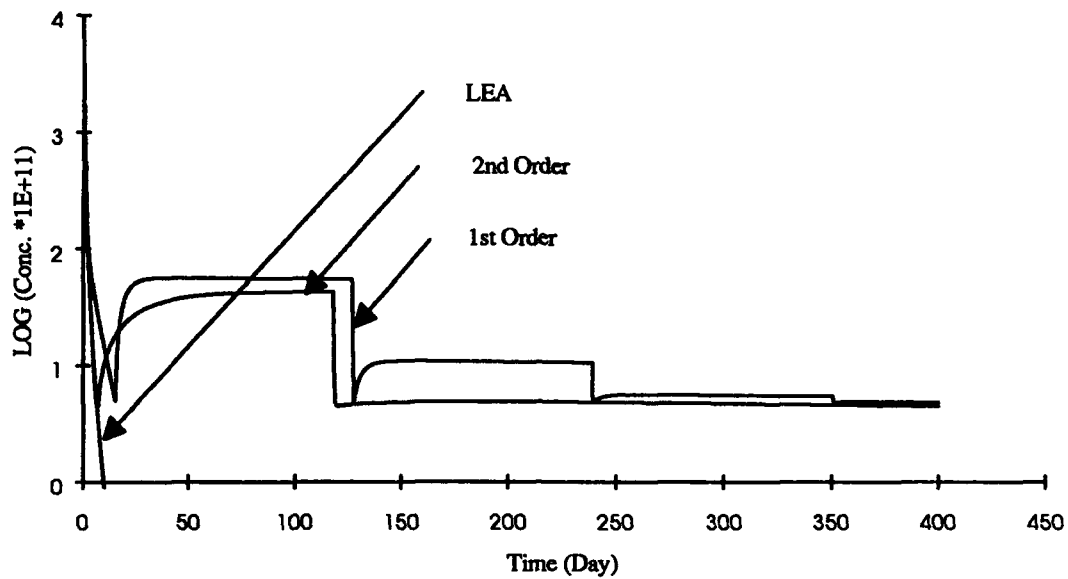


Figure D.3. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.009$)

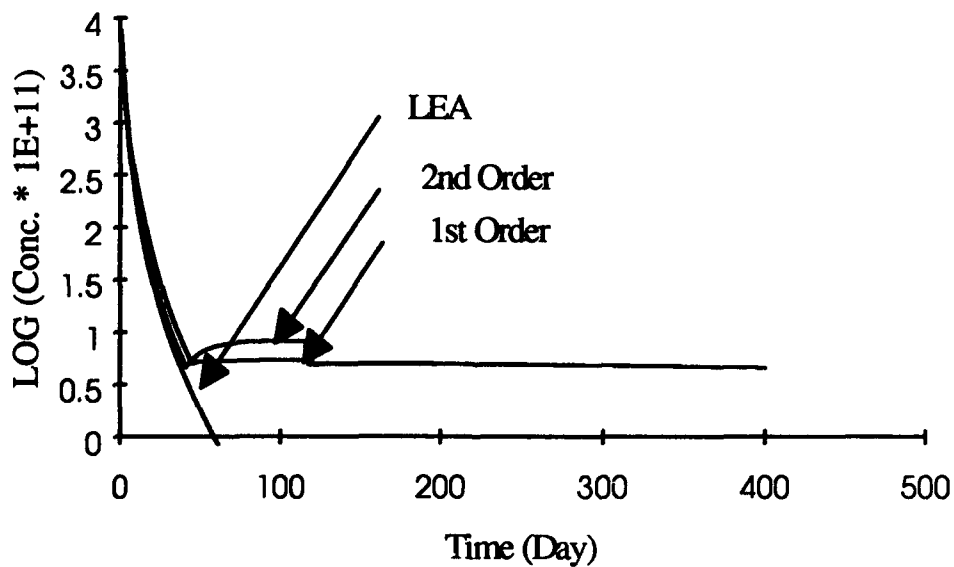


Figure D.4. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.013$)

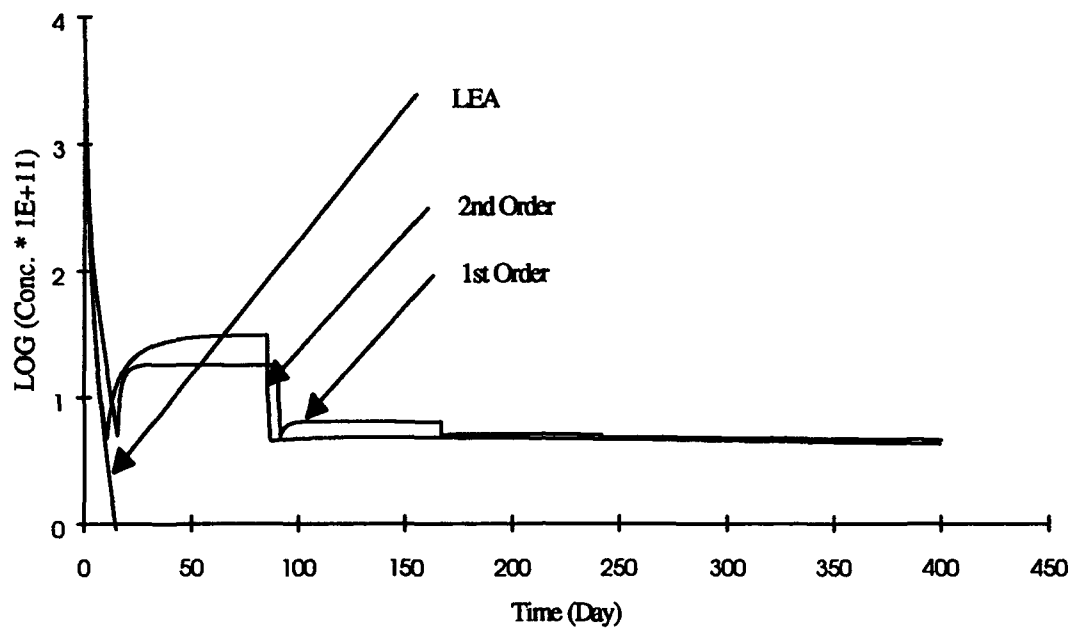


Figure D.5. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.013$)

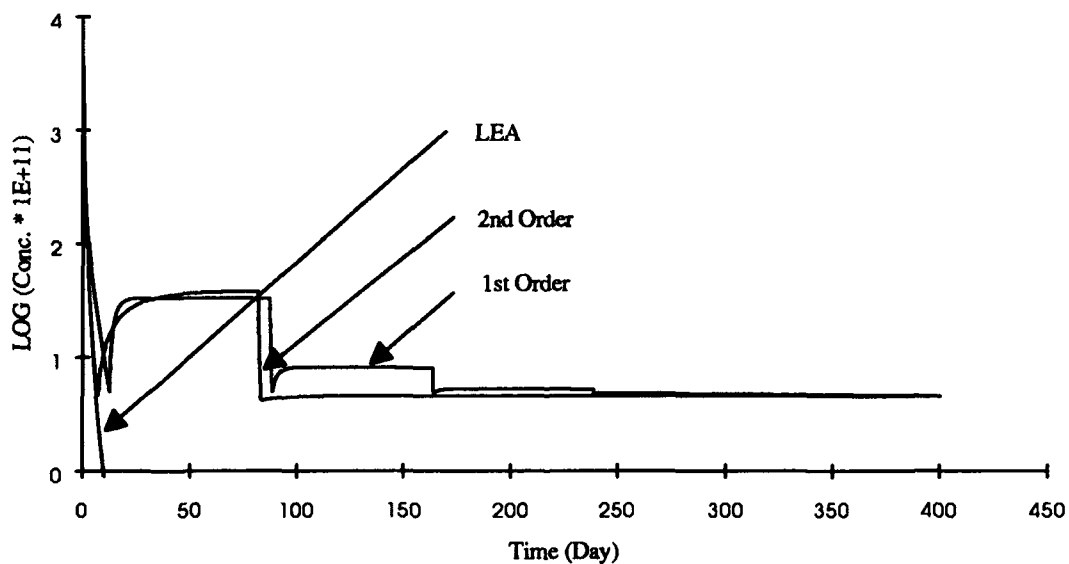


Figure D.6. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.013$)

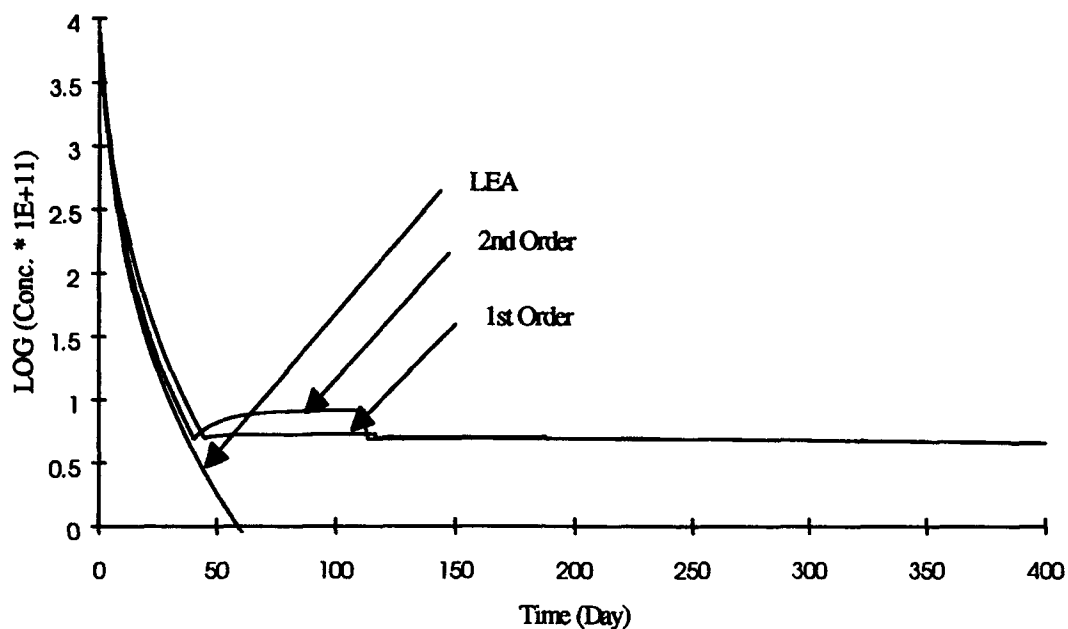


Figure D.7. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.014$)

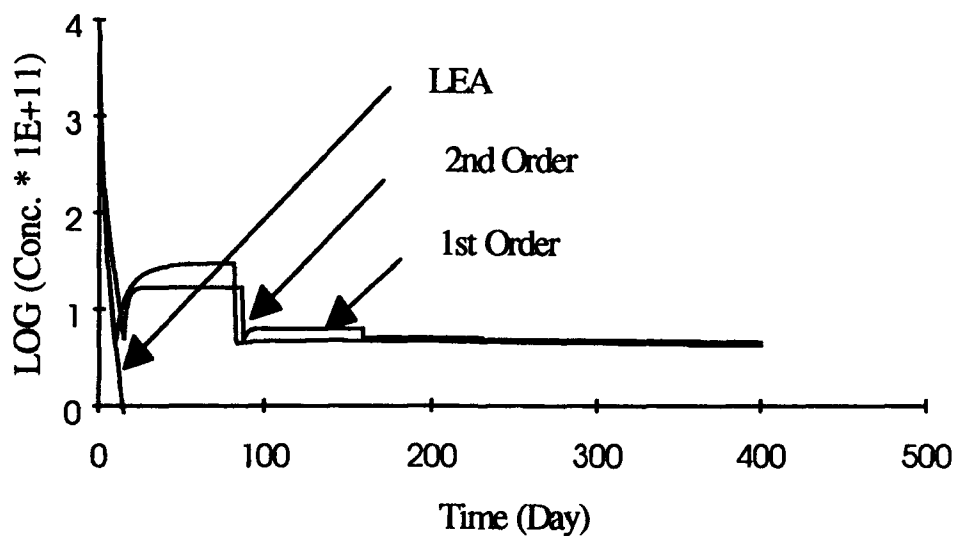


Figure D.8. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.014$)

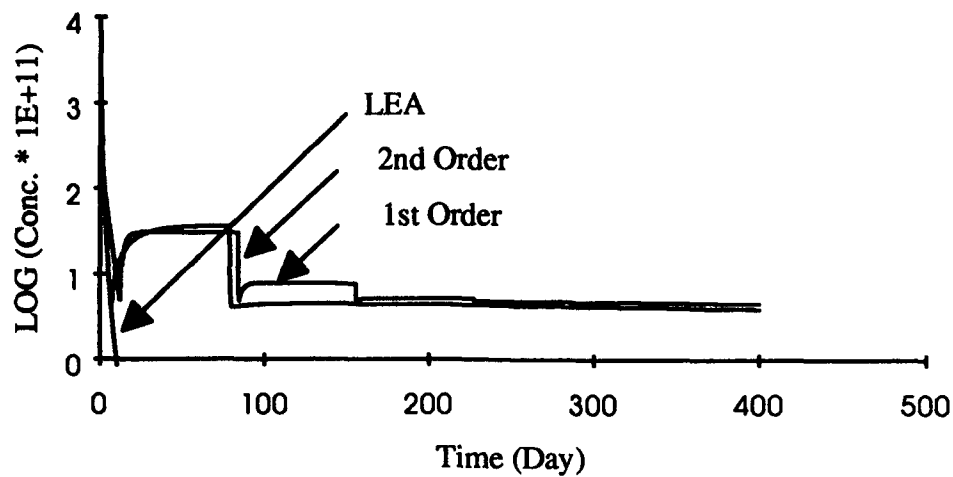


Figure D.9. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.014$)

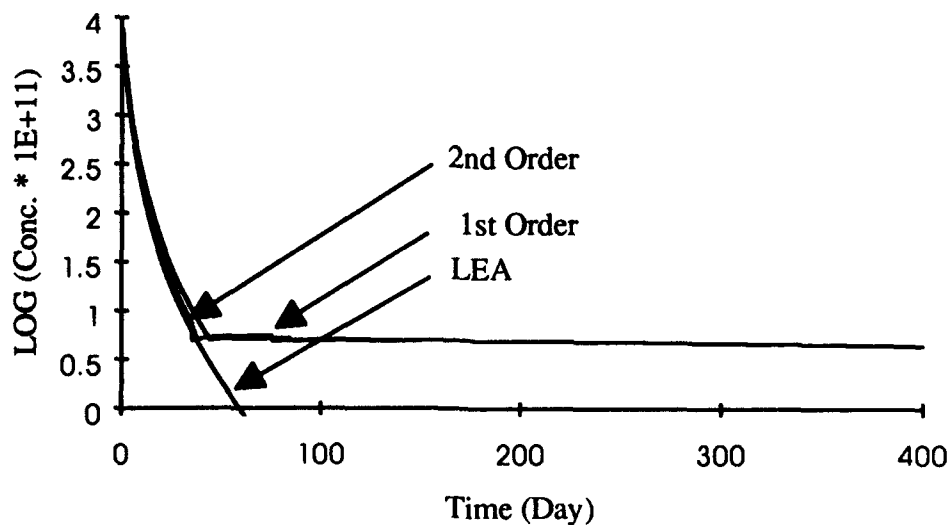


Figure D.10. Comparison of First- and Second Order Diffusion Models to LEA
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.025$)

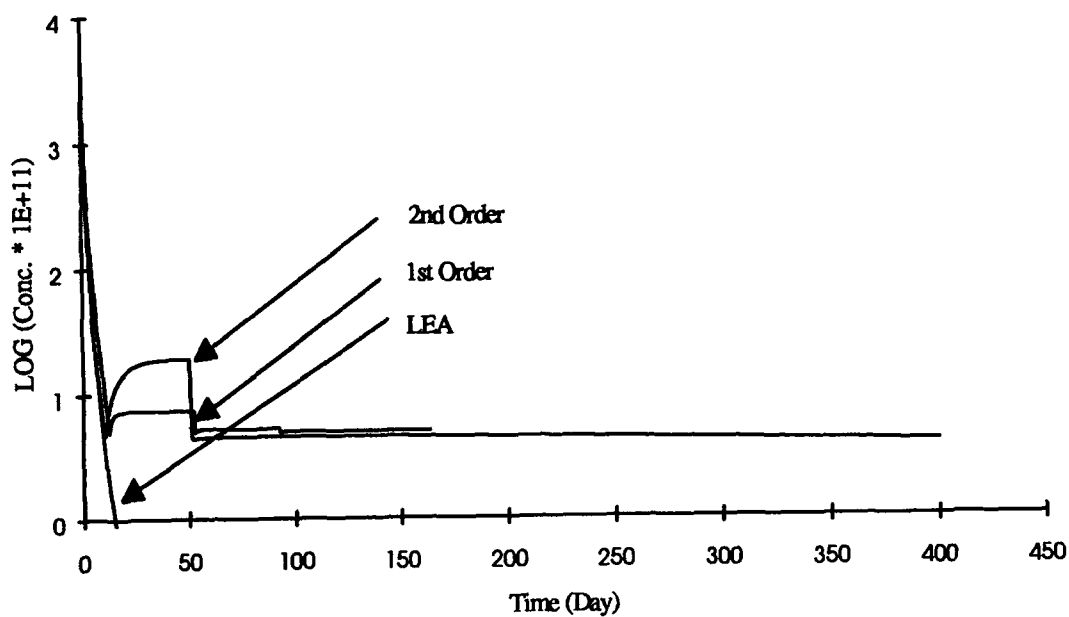


Figure D.11. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.025$)

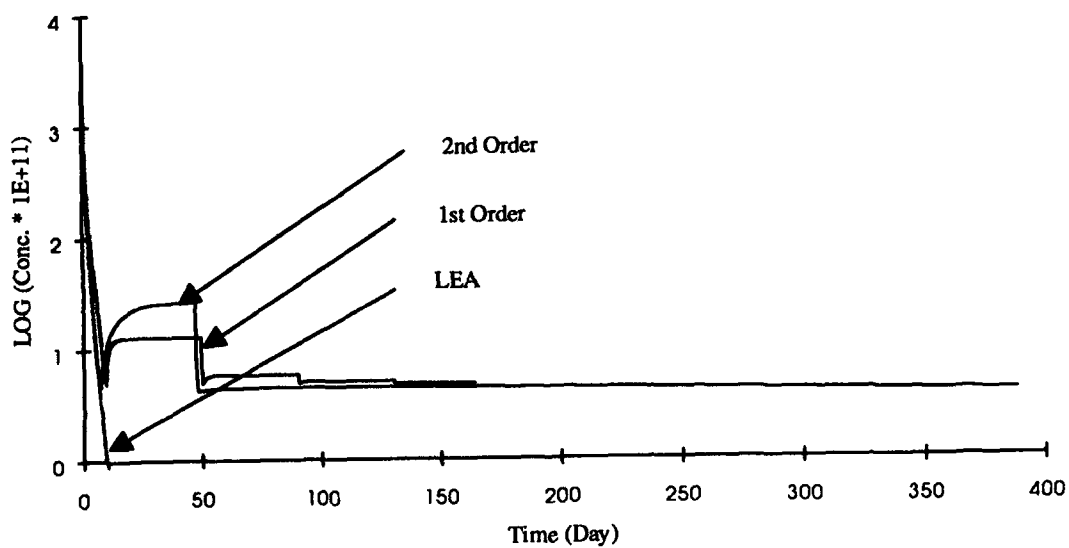


Figure D.12. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 600 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.025$)

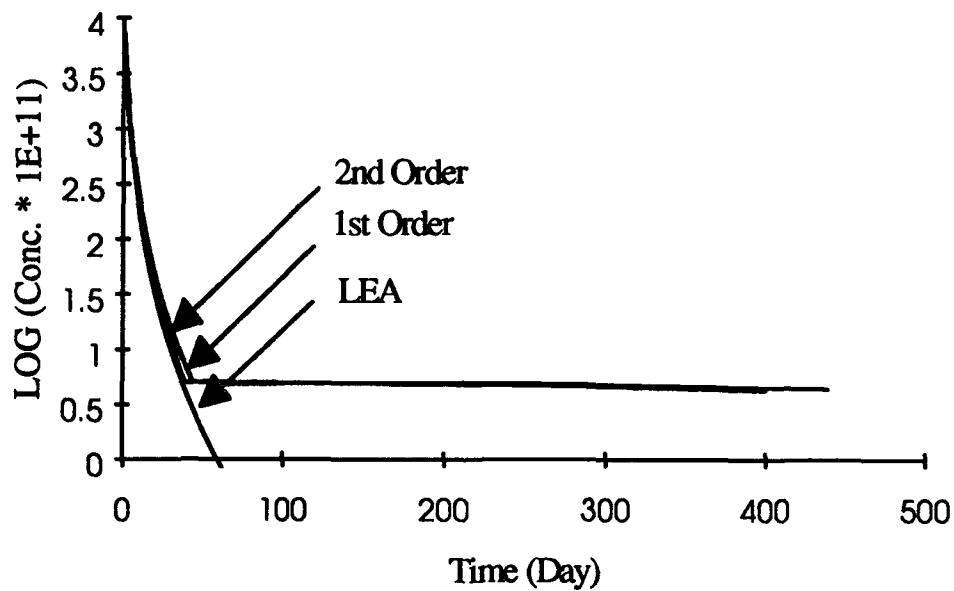


Figure D.13. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.039$)

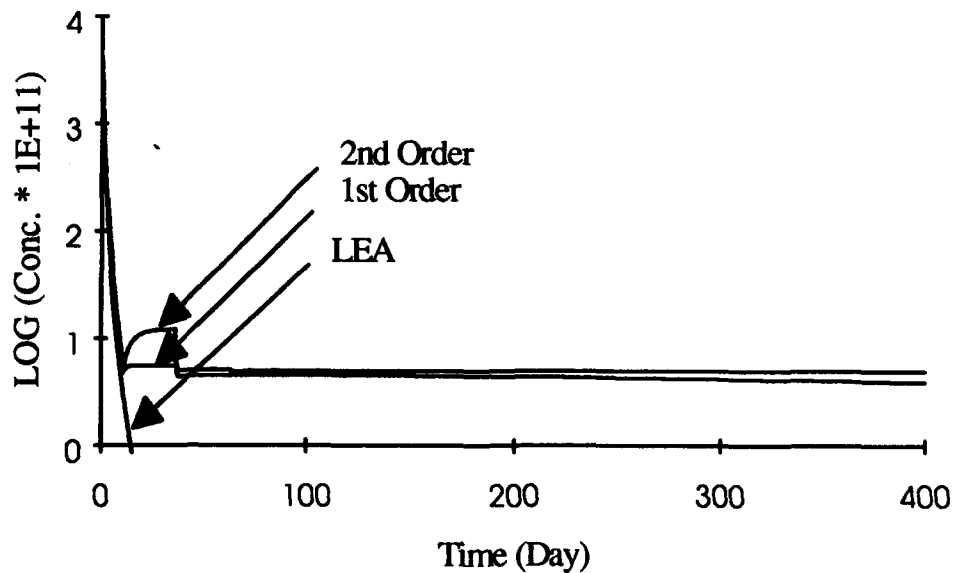


Figure D.14. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.039$)

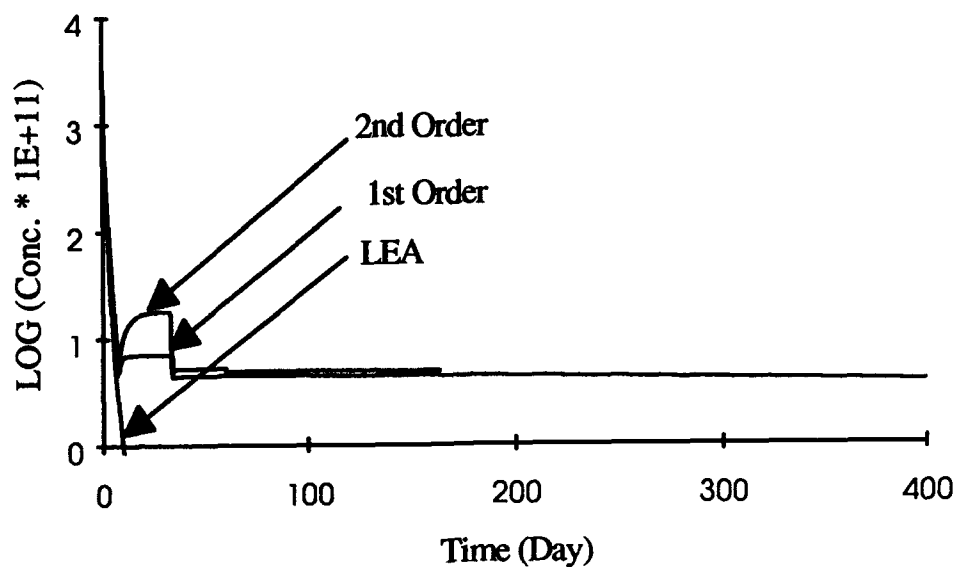


Figure D.15. Comparison of First- and Second-Order Diffusion Models to LEA
 $(Q = 600 \text{ m}^3/\text{day}) (D_e/a^2 = 0.039)$

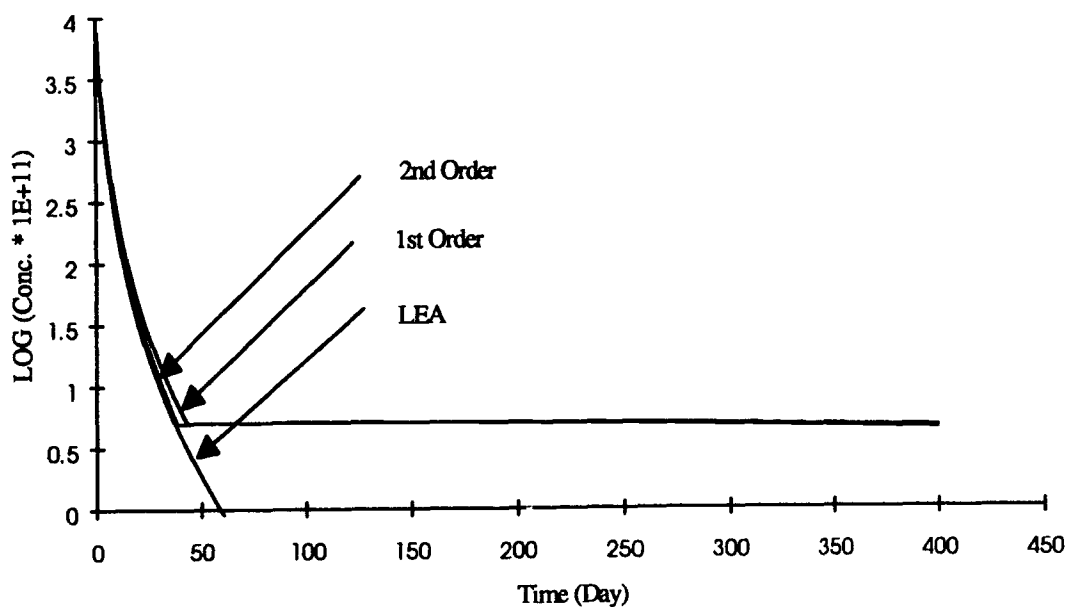


Figure D.16. Comparison of First- and Second-Order Diffusion Models to LEA
 $(Q = 100 \text{ m}^3/\text{day}) (D_e/a^2 = 0.12)$

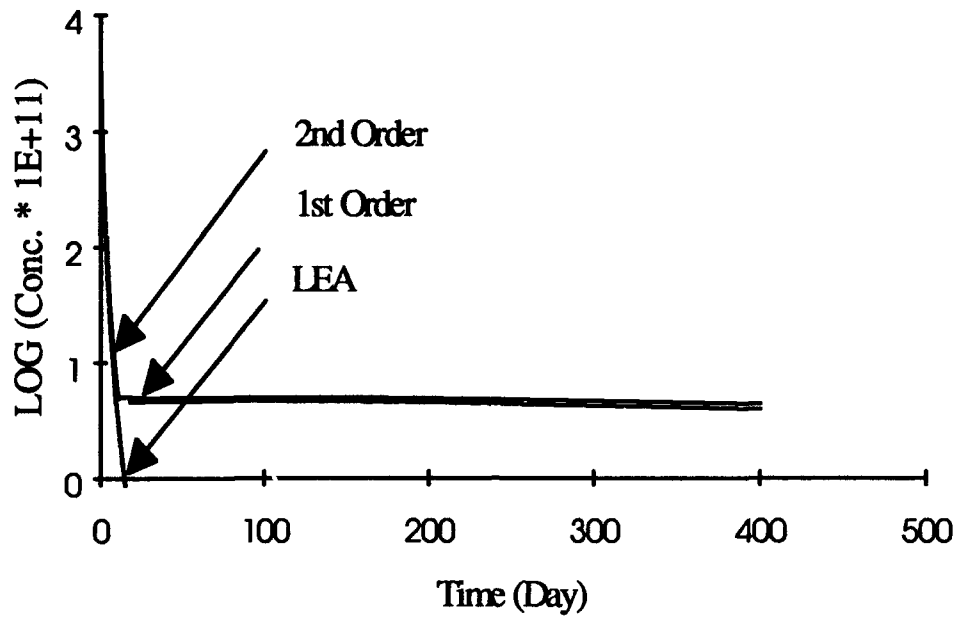


Figure D.17. Comparison of First- and Second-Order Diffusion Models to LEA
 $(Q = 400 \text{ m}^3/\text{day}) (D_e/a^2 = 0.12)$

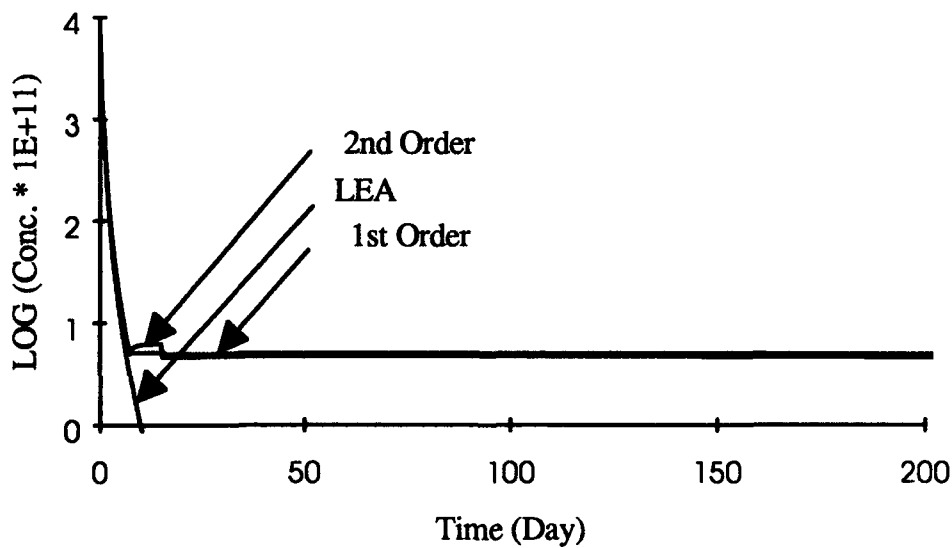


Figure D.18. Comparison of First- and Second-Order Diffusion Models to LEA
 $(Q = 600 \text{ m}^3/\text{day}) (D_e/a^2 = 0.12)$

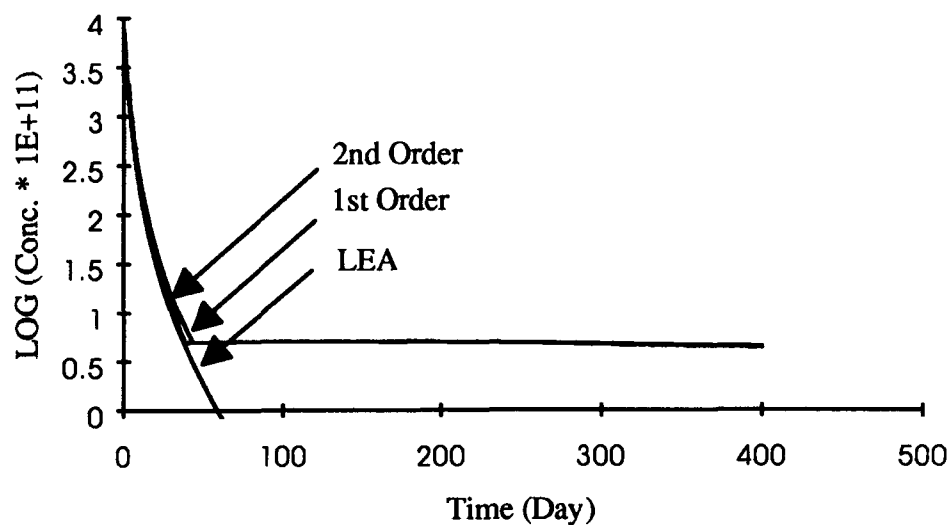


Figure D.19. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 100 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.225$)

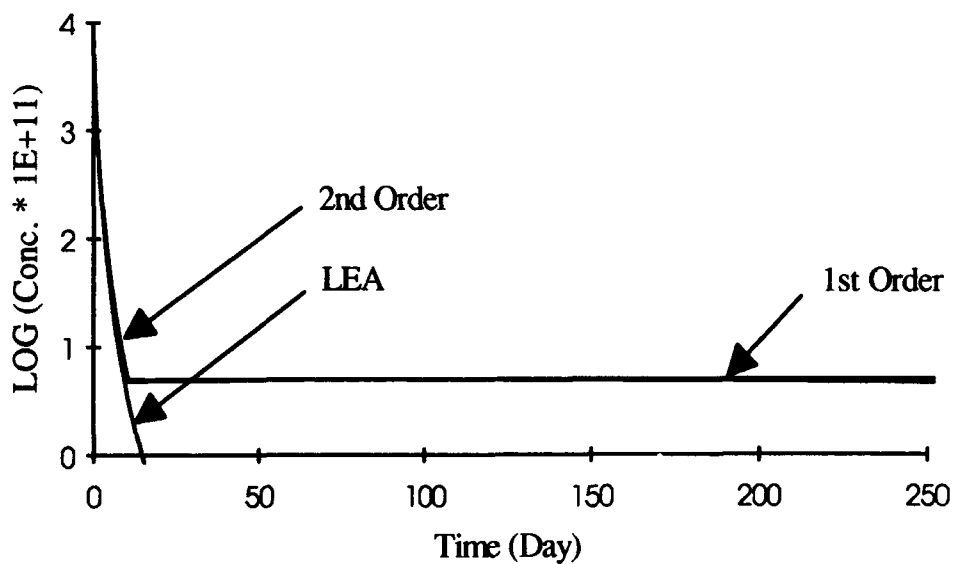


Figure D.20. Comparison of First- and Second-Order Diffusion Models to LEA
($Q = 400 \text{ m}^3/\text{day}$) ($D_e/a^2 = 0.225$)

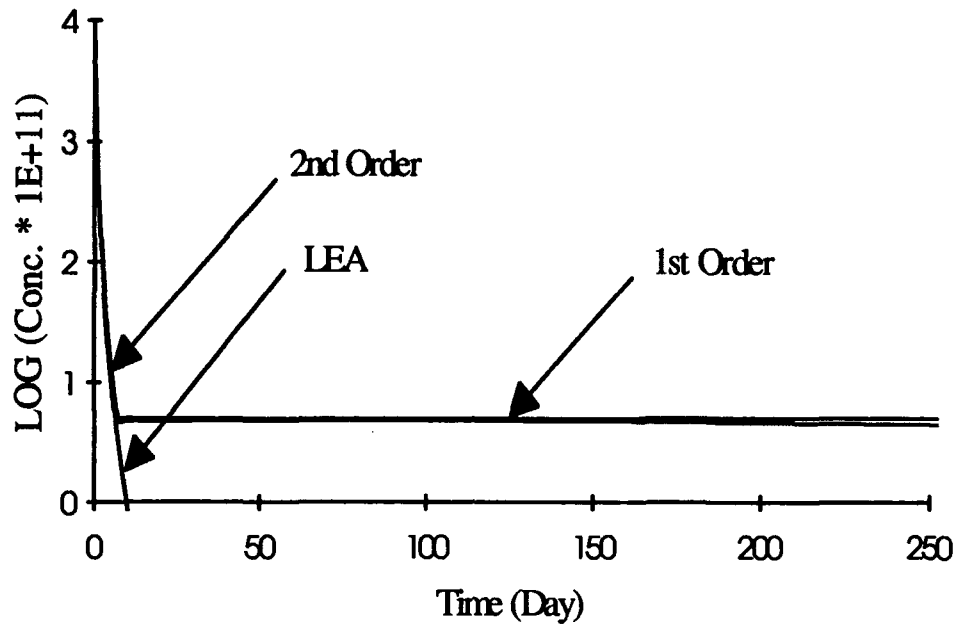


Figure D.14. Comparison of First- and Second-Order Diffusion Models to LEA
 $(Q = 600 \text{ m}^3/\text{day})$ $(D_e/a^2 = 0.225)$

Appendix E: First-Order Pulsed Pumping Strategies

1. Pulsed pumping times and rest (pump off) times are given in days for the various D_e/a^2 ratios and pumping rates studied for the first-order diffusion model. Cleanup Time is the total time to remediate the hypothetical aquifer to a level where rebound no longer exceeds the action level.

D_e/a^2	0.005	0.005	0.005	0.009	0.009	0.009
Q_w	100	400	600	100	400	600
Pump On	54.11	25.84	21.16	46.85	18.64	15.35
Pump Off	208.2	208.2	208.2	111.3	111.3	111.3
Pump On	2.13	1.82	1.5	0.4	1.24	1.06
Pump Off	208.2	208.2	208.2	111.3	111.3	111.3
Pump On	0.05	0.53	0.51	0.02	0.29	0.31
Pump Off	0	208.2	208.2	0	111.3	111.3
Pump On	0	0.04	0.07	0	0.02	0.04
Pump Off	0	0	0	0	0	0
Total On	56.29	28.23	23.24	47.27	20.19	16.76
Cleanup Time	472.69	652.83	647.84	269.87	354.09	350.66

D_e/a^2	0.013	0.013	0.013	0.014	0.014	0.014
Q_w	100	400	600	100	400	600
Pump On	45.2	15.45	12.5	45.08	15.13	12.21
Pump Off	75	75	75	71.4	71.4	71.4
Pump On	0.1	0.91	0.83	0.09	0.88	0.81
Pump Off	75	75	75	71.4	71.4	71.4
Pump On	0.02	0.17	0.21	0.02	0.16	0.2
Pump Off	0	75	75	0	71.4	71.4
Pump On	0	0.02	0.03	0	0.02	0.02
Pump Off	0	0	0	0	0	0
Total On	45.32	16.55	13.57	45.19	16.19	13.24
Cleanup Time	195.32	241.55	238.57	187.99	230.39	227.44

D_e/a^2	0.025	0.025	0.025	0.039	0.039	0.039
Q_w	100	400	600	100	400	600
Pump On	44.16	12.38	9.41	43.08	11.43	8.19
Pump Off	40.06	40.06	40.06	25.72	25.72	25.72
Pump On	0.07	0.46	0.52	0.07	0.19	0.29
Pump Off	40.06	40.06	40.06	25.72	25.72	25.72
Pump On	0.03	0.04	0.09	0.03	0.02	0.04
Pump Off	0	0	40.06	0	0	0
Pump On	0	0	0.02	0	0	0
Pump Off	0	0	0	0	0	0
Total On	44.26	12.88	10.04	43.18	11.64	8.52
Cleanup Time	124.38	93.00	130.22	94.62	63.08	59.96

D_e/a^2	0.12	0.12	0.12	0.225	0.225	0.225
Q_w	100	400	600	100	400	600
Pump On	43.33	10.79	7.28	43.11	10.67	7.16
Pump Off	8.33	8.33	8.33	4.45	4.45	4.45
Pump On	0.05	0.04	0.05	0.03	0.03	0.03
Pump Off	8.33	8.33	0	4.45	0	0
Pump On	0.02	0.02	0	0.02	0	0
Pump Off	8.33	0	0	0	0	0
Pump On	0.02	0	0	0	0	0
Pump Off	0	0	0	0	0	0
Total On	43.42	11.85	8.33	43.16	10.7	7.19
Cleanup Time	68.41	28.15	16.66	52.06	15.15	11.64

D_e/a^2	0.35	0.35	0.35
Q_w	100	400	600
Pump On	43.2	10.59	7.1
Pump Off	2.86	2.86	2.86
Pump On	0.03	0.02	0.02
Total On	43.23	10.61	7.12
Cleanup Time	46.09	13.47	9.98

Appendix F: Second-Order Pulsed Pumping Strategies

1. Pulsed Pumping times and rest (pump off) times are given in days for the various D_e/a^2 ratios and pumping rates studied for the second-order diffusion model. Cleanup time is the total time to remediate the hypothetical aquifer to a level where rebound no longer exceeds the action level.

D_e/a^2	0.005	0.005	0.005	0.009	0.009	0.009
Q_w	100	400	600	100	400	600
Pump On	41.1	9.9	6.7	39.5	10	6.8
Pump Off	208	208	208	111	111	111
Pump On	4.5	1.8	1.3	3	1.7	1.2
Pump Off	0	0	0	111	0	0
Pump On	0	0	0	0.2	0	0
Pump Off	0	0	0	0	0	0
Total On	45.6	11.7	11	42.7	11.7	8
Cleanup Time	253.6	219.7	219.0	264.7	122.7	119.0

D_e/a^2	0.013	0.013	0.013	0.014	0.014	0.014
Q_w	100	400	600	100	400	600
Pump On	41	10.1	6.8	40.1	10.1	6.8
Pump Off	75	75	75	71.5	71.5	71.5
Pump On	1.7	1.5	1.2	1.9	1.5	1.2
Pump Off	0	0	0	0	0	0
Pump On	0	0	0	0	0	0
Pump Off	0	0	0	0	0	0
Total On	42.7	11.6	8	42	11.6	8
Cleanup Time	117.7	86.6	83	113.5	83.1	79.5

$D_e/a^2 =$	0.025	0.025	0.025	0.039	0.039	0.039
Q_w	100	400	600	100	400	600
Pump On	39	10.2	6.9	38.6	10.1	6.9
Pump Off	40	40	40	26	26	26
Pump On	0.5	1.2	1	0.2	0.9	0.8
Pump Off	0	0	0	0	0	0
Pump On	0	0	0	0	0	0
Pump Off	0	0	0	0	0	0
Total On	39.5	11.4	7.9	38.8	11	7.7
Cleanup Time	79.5	51.4	47.9	64.8	37.0	33.7

D_e/a^2	0.12	0.12	0.12	0.225	0.225	0.225
Q_w	100	400	600	100	400	600
Pump On	38.4	9.6	6.5	38.3	9.5	6.5
Pump Off	0	8.3	8.3	0	0	0
Pump On	0	0.2	0.3	0	0	0
Pump Off	0	0	0	0	0	0
Pump On	0	0	0	0	0	0
Pump Off	0	0	0	0	0	0
Total On	38.4	9.8	6.8	38.3	9.5	6.5
Cleanup Time	38.4	18.1	15.1	38.3	9.5	6.5

D_e/a^2	0.35	0.35	0.35
Q_w	100	400	600
Pump On	37.7	9.5	6.5
Pump Off	0	0	0
Total On	37.7	9.5	6.5
Cleanup Time	37.7	9.5	6.5

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Vita

Major Jeffrey L. Caspers was born in Montevideo, Minnesota on 3 July 1957. On 15 March 1975 he enlisted in the United States Army National Guard. Later, he transferred to the Naval Reserve and entered active service for the first time eventually rising to the enlisted grade of Yeoman (Seaman). Upon receiving a full scholarship from the NROTC program, he transferred to the Marine Corps Reserve. He graduated from the University of Minnesota's Institute of Technology with a Bachelor of Civil Engineering degree in August 1979. Immediately thereafter he was commissioned a Second Lieutenant in the United States Marine Corps. Following, initial officer training he deployed with 2nd Battalion, 10th Marines from Camp Lejeune, North Carolina. overseas to Panama, the Caribbean, and Norway. Following this tour, he was assigned as the Atlantic Fleet Naval Gunfire Officer to the Staff of Commander, Amphibious Group Two in Norfolk, Virginia in 1982. There he planned and executed numerous Brigade and Division level landings in Europe, the Middle East and the Atlantic for both contingencies and exercises. Following advanced artillery training in 1984 he served successively as the 10th Marines Regimental Artillery Safety Manager and as a Battery Commander of a self-propelled artillery battery in 5th Battalion, 10th Marines. In 1987 he was transferred to Marine Corps Security Force Company, London, United Kingdom, serving both as Executive Officer and Commanding Officer of the counter-terrorism company assigned to the Commander in Chief, US. Naval Forces Europe Headquarters. In 1980, he served as the Fire Support Officer for Task Force Ripper, 1st Marine Division during Operations Desert Shield and Storm, earning the Navy Commendation Medal with valor device for operations in the vicinity of Kuwait City. On return to the United States, he became the Operations Officer (S-3) for 3d Battalion, 11th Marines, eventually

deploying overseas once again in 1992 for Operation Restore Hope to Mogadishu, Somalia. There he was the Operations Officer for Team Secure , a 3500-man, multi-service and international brigade of forces from seven different nations, earning the Meritorious Service Medal for coordinating and planning their activities in combat operations to secure the city. Major Caspers is married to the former Anita Van Timmeren of Yorktown, Virginia and they have four sons, Philip, Jonathan, Matthew and David. His next assignment will be as the Deputy for Environmental Affairs at Marine Corps Base, Camp Pendleton, California.

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13. ABSTRACT (Maximum 200 words)

This research postulates and demonstrates incorporating rate-limited sorption effects in the USGS SUTRA code for cleanup of a hypothetical sandy aquifer by pump-and-treat remediation methods. Contaminant transport is assumed to be affected by advection, dispersion, and rate-limited sorption/desorption. Sorption is assumed to be either equilibrium or rate-limited, with the rate-limitation described by either a first-order law, or by Fickian diffusion of contaminant through a spherical immobile pore region. Solutions are arrived at by split operator methods for the transport and one-dimensional Galerkin solutions for the solute concentration equations. The resulting model is tested against an analytical Laplace transform model for both first-order and Fickian diffusion methods in a radial pumping simulation. Model simulations are used to evaluate equilibrium, first-order and Fickian diffusion effects for pulsed and continuous pumping solutions within a hypothetical sandy aquifer. These show that equilibrium methods under-predicted rebound while first-order methods may both under-and over-predict rebound within the matrix for certain regions and may be equivalent to Fickian diffusion in equilibrium regimes for cleanup time prediction. Model simulations are then used to show the efficiency of pulsed pumping methods in cleanup mass extraction per pumped volume for a contaminated aquifer pump-and-treat remediation activity versus more conventional, continuous pumping methods.

14. SUBJECT TERMS

Physical Non-Equilibrium, Rate-Limited Sorption, Fickian Diffusion,
 SUTRA, Pump-and-Treat, Pulsed Pumping

153

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